

The simultaneous evaporation and imbibition of a droplet
on a porous substrate

PhD Thesis

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Abstract

Mathematical models for the evolution of, and deposition from, a thin particle-laden droplet on three different porous substrates undergoing simultaneous evaporation and imbibition are formulated and analysed. In particular, analytical expressions for the evolution of the droplet, the flow within the droplet and the substrate, and for the transport and deposition onto the substrate of the particles, are obtained for droplets evolving in four different modes. While the physical mechanisms driving evaporation (namely, the diffusion-driven transport of vapour in the atmosphere away from the free surface of the droplet) and imbibition (namely, the pressure-driven transport of liquid in the substrate away from the base of the droplet) are rather different, perhaps rather unexpectedly, it is found that there are a number of qualitative and quantitative similarities as well as differences in the resulting behaviour of the droplet as it loses mass to its environment. For example, it is shown that a droplet undergoing pure imbibition on an infinitely thick, isotropic, flooded, porous substrate or a finitely thick, anisotropic, flooded, porous substrate in the constant contact radius (CR) mode never completely imbibes (i.e., it has an infinitely long lifetime), but if it evaporates (either with or without imbibition also occurring) then it has a finite lifetime, and increasing the strength of evaporation and/or imbibition shortens its lifetime. It is also shown that in the regime in which diffusion of particles is faster than axial advection but slower than radial advection of particles for an infinitely thick, isotropic, flooded, porous substrate, the final deposit of particles left behind on the substrate after the droplet has completely evaporated and/or imbibed is independent of both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet. On the other hand, for a finitely thick, anisotropic, dry or flooded, porous substrate, this is

not the case. Not only are these results of theoretical interest, but they may also be potentially relevant to a wide variety of practical applications, including ink-jet printing, DNA chip manufacturing, and disease diagnostics, that would benefit from an improved ability to predict and/or control the final deposit pattern from a droplet undergoing simultaneous evaporation and imbibition.

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Chapter 1

Introduction

1.1 Motivation

The evaporation of a sessile droplet on a solid or porous substrate is not only of fundamental scientific interest but is also of importance in a wide variety of practical applications, such as printing onto paper and textiles (see, for example, Chen *et al.* [12]), paintwork restoration (see, for example, Zenit [13]), and microfabrication (see, for example, Tseng *et al.* [14]). Consequently, there have been extensive experimental, numerical, and/or theoretical investigations of the evaporation of a droplet on a solid substrate (see, for example, the review articles by Brutin & Starov [15], Gelderblom *et al.* [16], Wilson & D'Ambrosio [17], and Dombrovsky *et al.* [18]) and of the imbibition of a droplet on a porous substrate (see, for example, the review articles by Daniel & Berg [19], Gambaryan-Roisman [20], and Johnson *et al.* [21]) in a variety of different contexts. However, thus far there have been relatively few experimental, numerical, and/or theoretical investigations of a droplet undergoing simultaneous evaporation and imbibition on a porous substrate.

The aims of this thesis are to develop and analyse mathematical models that describe the evolution of, flow within, and deposition of particles from a thin sessile particle-laden droplet undergoing simultaneous evaporation and imbibition. This addresses a knowledge gap within the current literature, in which evaporation and imbibition have largely been studied in isolation. Specifically, throughout this thesis, we

use an approach based on lubrication theory (see, for example, Oron *et al.* [22], Craster & Matar [23], and Davis [24]) to formulate and analyse our mathematical models.

The following sections introduce a sessile droplet and porous substrate, and review the relevant literature on evaporation, imbibition, and their simultaneous occurrence. These sections highlight the physical mechanisms, modelling approaches, and key previous results that provide the context for the aims of this thesis. We then examine particle transport and the well-known coffee-ring effect, summarise the associated literature in this area, and outline strategies proposed to suppress the coffee-ring effect. The chapter concludes with an overview of the thesis and a summary of the publications and presentations arising from the present work.

1.2 A Sessile Droplet

A sessile droplet is a finite volume of liquid that is sitting on the surface of a substrate. The liquid makes contact with the surface of the substrate and the atmosphere along the droplet-substrate interface (i.e., the base of the droplet) and droplet-atmosphere interface (i.e., the free surface of the droplet), respectively. The contact angle of a droplet is formed at the three-phase boundary (i.e., the contact line) between the surface of the substrate, the atmosphere, and the free surface of the droplet. Specifically, the contact angle is the angle formed between the surface tangent on the liquid-vapour interface and the tangent on the solid-liquid interface, measured from inside the liquid. Figure 1.1 shows an image of sessile water droplets on a solid (steel) substrate. We note that, in general, the contact angle can vary along the contact line of the droplet, such as for asymmetric sessile droplets. Throughout this thesis we will only consider the situation of axisymmetric sessile droplets in which the contact angle is constant in space (but not necessarily in time) along the contact line. When a sessile droplet is axisymmetric, the radius of the (circular) footprint of the droplet on the substrate is referred to as the contact radius of the droplet. Throughout this thesis, we analyse droplet evolution in four modes of evaporation and/or imbibition, namely the constant radius (CR), constant angle (CA), Stick-Slide (SS), and Stick-Jump (SJ) modes, as

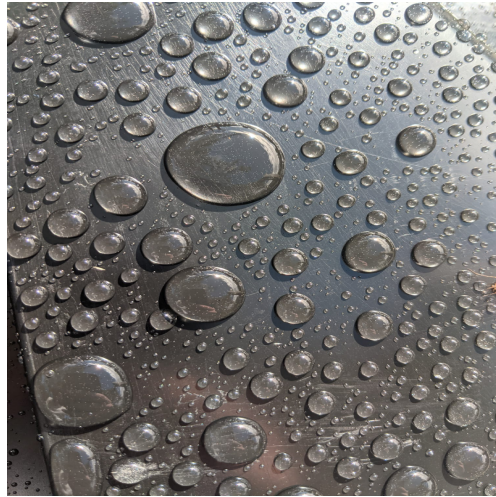


Figure 1.1: Image of sessile water droplets resting on a solid (steel) substrate. Photograph courtesy of Callum Bruce Bell.

discussed in Section 2.5.

The evolution of sessile droplets is typically measured experimentally using optical imaging, enabling precise measurement of the droplet geometry over time. Side-view imaging, often combined with backlighting, allows extraction of the contact angle, contact radius, and free surface via image analysis algorithms, while top-view imaging provides planform area and symmetry information. High-speed cameras are employed to capture rapid changes in contact-line position and interferometric techniques can resolve subtle variations in free-surface curvature (see, for example, Edwards *et al.* [25]). The flow fields within evaporating and/or imbibing droplets are visualised using particle image velocimetry (PIV) or particle tracking velocimetry (PTV), in which tracer particles are illuminated by a laser sheet and imaged at high frame rates to reconstruct velocity trajectories (see, for example, Jaijus & Singh [26]). Confocal and fluorescence microscopy enable three-dimensional mapping of flow structures, revealing vertical circulation patterns and stratification effects (see, for example, Li & Hong [27]). More advanced approaches, such as optical coherence tomography (OCT) and light-sheet microscopy, permit observation of near-surface flows and bulk circulation without significant optical distortion due to interface curvature (see, for example, Manukyan *et al.* [28]). These measurements are essential for quantifying evaporation and/or imbibition.

tion and validating theoretical models of droplet evolution on various substrates.

1.3 A Porous Substrate

A porous substrate is a material which contains pores (i.e., voids). The skeletal portion of a porous substrate is often referred to as the matrix or frame of the substrate. The substrate consists of pore space that permits the ingress, transport, and storage of liquids and/or gases. Natural porous substrates include soils (such as sand and gravel), rocks (such as basalt and pumice), gemstones (such as amber and pearl), biological tissues (such as bone, wood, and cork), and everyday household materials (such as paper, tissues, and sponges). Synthetic porous substrates include engineered cements and ceramics (such as ceramic foams), sintered-metal and activated-carbon filters, polymer and ceramic membranes, aerogels, metal–organic frameworks, hydrogels, and non-woven fabric mats.

Modelling the transport of liquid within porous substrates presents significant challenges due to the microstructural heterogeneity of the pore network. At the pore (i.e., microscopic) scale, the geometry and connectivity of individual pores can vary significantly. Directly capturing these variations requires detailed microstructural characterisation and computationally expensive simulations, such as pore-scale network models (see, for example, Li *et al.* [29] and Yin *et al.* [30]). At the continuum (i.e., macroscopic) scale, Darcy’s law provides a representation of the flow within a porous substrate by averaging the underlying pore-scale behaviour (see, for example, Larson [31] and Whitaker [32]). In his original work, Darcy [33] investigated the flow of liquid through flooded porous sand columns, deriving an empirical relationship between volumetric flux and pressure gradient. More than a century later, Whitaker [32] derived a theoretical variant of Darcy’s law directly from the Navier–Stokes equations using a formal averaging procedure. Darcy’s law is mathematically analogous to other linear transport laws, including Fourier’s law for heat conduction, Ohm’s law for electrical conduction, Fick’s law for molecular diffusion, and Hagen–Poiseuille’s law for laminar flow through cylindrical tubes (see, for example, Bear [34]).

In Section 2.7.1, we describe situations in which the porous substrate is modelled

as an infinitely thick, isotropic, flooded substrate with interconnected pores. In this context, the isotropy of the substrate means that flow occurs in both the radial and vertical directions. In Sections 2.7.2 and 2.7.3, we describe situations in which the porous substrate is modelled as thick, anisotropic, and either flooded or initially dry. In this context, anisotropy restricts flow to the vertical direction, making the substrate mathematically equivalent to an array of non-connected, vertically aligned capillary tubes of constant cross-section. In this framework, Darcy’s law can be interpreted as the macroscopic analogue of microscopic Hagen–Poiseuille flows through each capillary (see, for example, Davis & Hocking [35, 36]).

While the modelling assumption of non-connected, vertically aligned pores with constant cross-sectional area is, in most cases, an idealisation, it can provide an adequate representation of situations in which the net liquid transport within the substrate is predominantly vertical. This simplification reduces the complexity of the imbibition problem while retaining the essential physics governing the phenomenon. Furthermore, it offers a reasonable approximation for certain stratified or engineered substrates with limited pore connectivity, making it a physically relevant and informative case to consider. As an example, Figure 1.2 shows top and side-view images from Pack *et al.* [1], showing a porous substrate in which the pores are predominantly vertically aligned and non-connected, closely matching the idealised geometry assumed in the imbibition models described in Sections 2.7.2 and 2.7.3.

There are also the situations considered by some previous authors where the substrate is modelled as a thin, anisotropic porous substrate with interconnected pores which is initially flooded in the region within the initial footprint of the droplet. In this context, the anisotropy of the substrate means that flow occurs only in the radial direction (see, for example, Marmur *et al.* [37], Borhan & Rungta [38], Starov *et al.* [39], Hyväluoma *et al.* [40], Heinz *et al.* [41, 42], and Zheng [43]). While some preliminary work was carried out on this situation during the course of my PhD studies, these results are not included as part of this thesis.

Liquid transport within porous substrates is often visualised using dye-tracking, in which a coloured or fluorescent tracer is imbibed and imaged over time to mea-

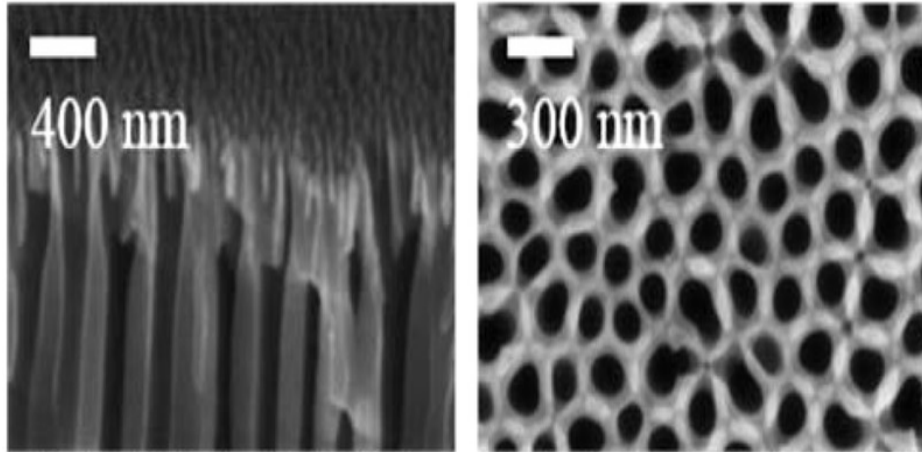


Figure 1.2: Top and side-view images of a nano-porous (anodic aluminium oxide) substrate. Adapted from Figure 1 of Pack *et al.* [1] with permission, Copyright 2015, from Langmuir.

sure the spatiotemporal evolution of liquid (see, for example, Desie & Van Roost [44]). For opaque or complex materials, neutron radiography and X-ray micro-computed-tomography (micro-CT) provide non-invasive, time-resolved imaging of saturation profiles (see, for example, Zhang *et al.* [45]). Optical methods such as light transmission or reflectance imaging can quantify local saturation in thin or semi-transparent substrates (see, for example, Bouchard & Chandra [46]). These measurements are essential for quantifying imbibition and validating theoretical models of liquid transport within porous substrates.

1.4 Droplet Evaporation on a Solid Substrate

Droplet evaporation is the process by which a liquid droplet loses mass into the surrounding atmosphere as molecules escape into the vapour phase. The rate at and manner in which this occurs depend on factors such as the properties of the liquid and surrounding environment. In this section, we describe the modelling approaches and key findings pertinent to the analysis within this thesis.

1.4.1 Diffusion-limited Evaporation

The theoretical study of the diffusion-limited evaporation of a droplet on a solid substrate was pioneered by Mangel & Baer [47], Picknett & Bexon [48], Birdi *et al.* [49], and Bourges-Monnier & Shanahan [50]. The diffusion-limited evaporation of a droplet is driven by the difference between the saturated concentration of vapour at the free surface of the droplet and the ambient concentration of vapour in the atmosphere. In Section 2.2 we provide a detailed description of the mathematical model for the diffusion-limited evaporation of a thin sessile droplet. In practice, the timescales for diffusion of vapour away from the free surface of the droplet and the adjustment of the free surface are both short compared to the typical lifetime of a droplet (see, for example, Larson [51]), and so both processes are often assumed to be quasi-steady. In their pioneering study, Picknett & Bexon [48] determined the evolution, and hence the lifetime, of evaporating droplets with pinned (fixed) and unpinned (receding) contact-lines. Many subsequent authors, such as Birdi *et al.* [49], Bourges-Monnier & Shanahan [50], Deegan [52], Deegan *et al.* [53, 54], Dunn *et al.* [55, 56], Hu & Larson [8, 57–59], Sultan *et al.* [60, 61], Masoud *et al.* [62], McHale *et al.* [63], Popov [64], Zheng *et al.* [65], Freed-Brown [66], Stauber *et al.* [67–69], Wray *et al.* [70–72], Moore *et al.* [73, 74], Schofield *et al.* [75, 76], Du & Deegan [77], Kang *et al.* [78], Boulogne *et al.* [79], Boulogne & Dollet [80], D’Ambrosio *et al.* [81–84], Gelderblom *et al.* [16], Seyfert *et al.* [85], Moore & Wray [86], Wray & Moore [87–89], Yariv [90], Erdem *et al.* [91], O’Brien *et al.* [92], Mei & Zhou [93], and Jeon *et al.* [94] have built on the work of Picknett & Bexon [48] to obtain exact, asymptotic, approximate, and/or numerical descriptions of the evolution, and hence the lifetime, of droplets undergoing diffusion-limited evaporation in a variety of different situations.

Notably, Dunn *et al.* [56] experimentally and theoretically investigated the evolution of thin evaporating sessile droplets with pinned contact lines. The authors extended the basic diffusion-limited model to include the influence of substrate thermal conductivity by coupling vapour concentration in the surrounding atmosphere with temperature variations in the liquid and substrate through the temperature dependence of the saturation concentration, and showed that droplet lifetime increases with substrate thermal

conductivity. Their model gave good quantitative agreement with experimental evaporation rates for acetone and methanol, although it under-predicted rates for water. The authors then incorporated Newton’s law of cooling on the non-wetted substrate surface and buoyancy effects of the vapour, resulting in excellent quantitative agreement for all three liquids on both aluminium and PTFE substrates. Later, Wray *et al.* [71] theoretically investigated the evaporation of multiple thin sessile droplets with pinned and unpinned contact lines. The authors considered the “shielding effect”, whereby the droplets reduce each other’s evaporation rate and thus extend each other’s lifetimes. Comparisons with numerical solutions for two identical droplets showed excellent agreement even beyond the formal range of validity (i.e., well separated droplets), including in the limit of touching droplets. Additionally, comparison with experimental data for seven water droplets in an I-shaped array obtained by Khilifi *et al.* [95] was in quantitative agreement, with the central droplet strongly shielded and the corner droplets weakly shielded. Recently, Wray & Moore [87] theoretically investigated the evolution of, flow within, and deposition from thin sessile non-circular particle-laden droplets with pinned contact lines. The authors developed a novel asymptotic solution to the mixed boundary value problem for vapour concentration, valid up to second order for small perturbations to a circular footprint. Although formally derived for nearly-circular droplets, the method was shown to accurately predict evaporative fluxes for a wide range of regular and non-regular polygon shapes, such as triangles, squares, rectangles, and five-pointed stars, in excellent agreement with direct numerical simulations. Additionally, the authors also considered large, gravity-dominated, particle-laden droplets and demonstrated that variations in contact-line curvature enhance deposition in high-curvature regions and suppress it in low-curvature regions, consistent with previous studies on particle deposition in evaporating droplets.

1.4.2 One-sided Evaporation

There are situations in which the diffusion-limited evaporation model does not adequately describe the underlying physics of droplet evaporation, such as when the vapour phase is fully saturated or the substrate is strongly heated. The theoretical study of

the so-called one-sided evaporation of a droplet on a solid substrate was pioneered by Burelbach *et al.* [96]. The one-sided evaporation of a droplet is driven by the rate of transfer of molecules across the free surface boundary. Specifically, the one-sided model assumes that the density, viscosity, and thermal conductivity of the atmosphere are small compared to those of the liquid. In their pioneering study, Burelbach *et al.* [96] derived the one-sided model and considered the evaporation of a liquid film on a heated substrate. Many subsequent authors such as Anderson & Davis [97], Oron *et al.* [22], Warner *et al.* [98], Ajaev [99], Ajaev *et al.* [100], Murisic & Kondic [101], Cazabat & Guéna [102], Maki & Kumar [103], Karapetsas *et al.* [104], Ajaev & Kabov [105], Charitatos *et al.* [106,107], Pham & Kumar [108,109], Kumar & Charitatos [110], and Larsson & Kumar [111,112] have built on the work of Burelbach *et al.* [96] to obtain exact, asymptotic, approximate, and/or numerical descriptions of the evolution, and hence the lifetime, of droplets undergoing one-sided evaporation in a variety of different situations. Furthermore, there are generalised models that incorporate both diffusion-limited and one-sided droplet evaporation as limiting cases (see, for example, Sultan *et al.* [61] and Hartmann *et al.* [113]). In particular, Hartmann *et al.* [113] considered the evolution of a confined volatile sessile droplet and adopted a thin-film approach formulated within the framework of gradient dynamics.

The studies described in this section provide a comprehensive understanding of the evaporation of a sessile droplet on a solid (i.e., non-porous) substrate, establishing the physical mechanisms and modelling approaches relevant to evaporating sessile droplets. In this thesis, evaporation is not treated in isolation, instead, it forms one part of the simultaneous problem with imbibition, whose combined influence on droplet evolution, flow, particle transport, and deposit formation is the central focus of this work. Throughout this thesis, we only consider the basic diffusion-limited evaporation model, although the lubrication-based approach developed in Section 2.4 can, in principle, also accommodate extensions to the diffusion-limited evaporation model or the one-sided evaporation model.

1.5 Droplet Imbibition on a Porous Substrate

Imbibition is the process by which a liquid on a porous substrate is absorbed into the substrate through its network of pores. The rate and manner in which this occurs depend on factors such as the pore structure, wettability, and saturation state of the substrate. In this section, we describe the modelling approaches and key findings pertinent to the analysis within this thesis.

1.5.1 A Flooded Porous Substrate

The theoretical study of the imbibition of a droplet on a flooded porous substrate was pioneered by Davis & Hocking [35]. The imbibition of a droplet is driven by the difference between the pressure within the droplet and the capillary pressure within the substrate. When the porous substrate is flooded there are no liquid-air interfaces, and therefore no capillary pressure, within the substrate, and hence the imbibition is driven by the difference between the pressure within the droplet and atmospheric pressure. In practice, the timescales for the transport of liquid away from the base of the droplet and the adjustment of the free surface are both short compared to the typical lifetime of a droplet (see, for example, Davis & Hocking [35]) and so, as in the evaporative problem described in the previous section both processes are often assumed to be quasi-steady. Davis & Hocking [35] considered several situations involving the imbibition of a thin two-dimensional droplet. Specifically, they considered the evolution of such droplets on both horizontal and inclined porous substrates, where the pores within the substrate were either interconnected or non-connected and vertically aligned. In a companion paper, Davis & Hocking [36] considered several situations involving (and related to) the imbibition of a thin two dimensional droplet on a finitely thick, anisotropic, initially dry, porous substrate, as discussed in Section 1.5.2.

In contrast to the large body of work on the evaporation of droplets on solid substrates, relatively few subsequent authors (with the exception of Starov *et al.* [114], Alleborn & Raszillier [115], and Espín & Kumar [2]) have built on the work of Davis & Hocking [35, 36] to obtain asymptotic, approximate, and/or numerical descriptions

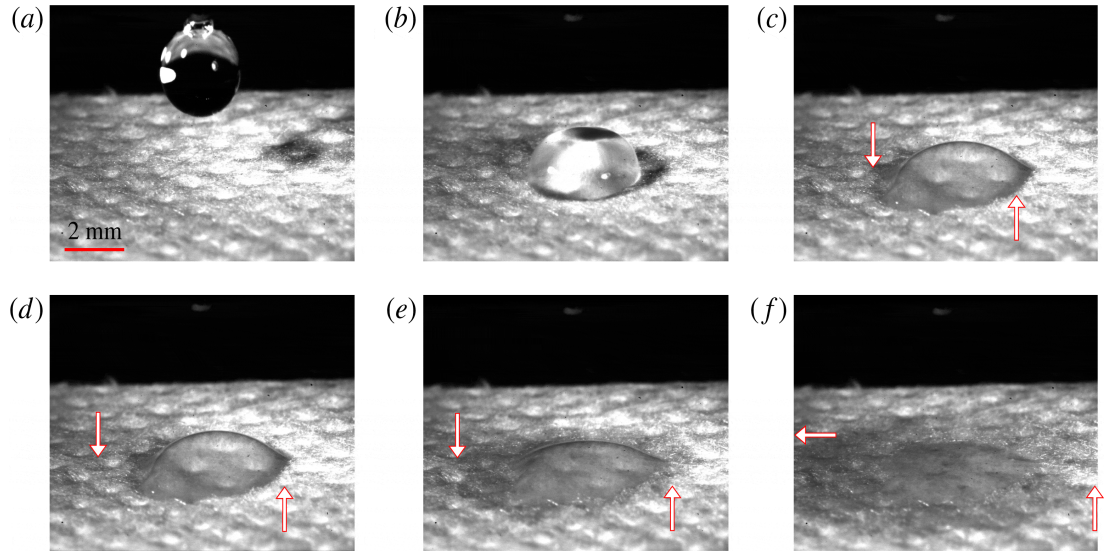


Figure 1.3: Images of a sessile water droplet with initial volume 11.13 mm^3 imbibing on a 0.214 mm thick, porous fibre mat at time (a) 0 s , (b) 0.104 s , (c) 0.212 s , (d) 0.312 s , (e) 0.412 s , and (f) 0.812 s . The arrows indicate the (approximate) furthest extent of liquid within the fibre mat. Reproduced from Figure 1 of Espín & Kumar [2] with permission, Copyright 2015, from Cambridge University Press.

of the evolution of a droplet undergoing imbibition on a flooded porous substrate. In a key study, Starov *et al.* [114] experimentally and theoretically investigated the simultaneous spreading and imbibition of a droplet on an anisotropic, flooded, porous substrate with a solid base, where the substrate is thin relative to the initial droplet height. The authors assumed that the flow within the substrate occurred only in the radial direction. The theoretical model was compared with experimental results and an empirical spreading coefficient was determined. Following this, Alleborn & Raszil-lier [115] theoretically investigated the simultaneous spreading and imbibition of a thin sessile droplet on a layered porous substrate. In a later contribution, Espín & Kumar [2] theoretically investigated the simultaneous spreading and imbibition of a thin sessile droplet on a finitely thick, anisotropic, flooded, porous substrate, where flow occurred only in the vertical direction. Specifically, Espín & Kumar [2] described the evolution of a droplet in the presence of intermolecular forces, a precursor film, disjoining pressure, and surface roughness. Figure 1.3 shows Figure 1 from Espín & Kumar [2], in which a sessile water droplet imbibes into a porous fibre mat with a pinned contact line.

1.5.2 An Initially Dry Porous Substrate

The theoretical investigation of droplet imbibition into an initially dry porous substrate was pioneered by Marmur [116,117] and Denesuk *et al.* [118]. In such systems, the advancing liquid forms a liquid–air interface within each pore, where the curvature of the meniscus generates a capillary pressure that draws liquid from the droplet into the substrate. This pore-scale mechanism is described by the Bell–Cameron–Lucas–Washburn equation, commonly referred to as the Washburn equation, which models the imbibition of a wetting liquid into a capillary tube or pore under the action of capillary forces (see, for example, Bell & Cameron [119], Lucas [120], Washburn [121], Denesuk *et al.* [118], and Marmur & Cohen [122]). The model predicts that the wetting front evolution is proportional to the square root of time, a scaling widely used to compare theoretical predictions with experimental measurements during droplet imbibition (see, for example, Gambaryan-Roisman [20]).

The validity of this scaling has been examined experimentally by numerous authors, including Desie & Van Roost [44], Kumar & Deshpande [123], Lee *et al.* [4], Léang *et al.* [3], and Tan [124]. While the degree of agreement varies, good quantitative agreement is typically observed in substrates with ordered, predominantly vertical, and non-connected pores where inertial effects are negligible (see, for example, Tan [124]). In contrast, substrates with disordered and interconnected pores tend to exhibit non-uniform wetting front evolution. Figure 1.4 shows a uniform wetting front within a colloidal silica substrate, as investigated by Léang *et al.* [3], whereas Figure 1.5 shows a non-uniform wetting front within a limestone substrate, as investigated by Lee *et al.* [4].

In their pioneering study Denesuk *et al.* [118] determined the evolution, and hence the lifetime, of an imbibing droplet on a finitely thick, anisotropic, initially dry, porous substrate with pinned (fixed) and unpinned (receding) contact lines. Many subsequent authors, such as, Danino & Marmur [125], Marmur & Cohen [122], Selim *et al.* [126], Middleman [127], Davis & Hocking [36], Bacri & Brochard-Wyart [128], Yip *et al.* [129], Clarke *et al.* [130], Holman *et al.* [131], Starov *et al.* [39,132], Hapgood *et al.* [133], Marmur [134], Alleborn & Raszillier [115,135,136], Desie *et al.* [137], Anderson [138], Desie

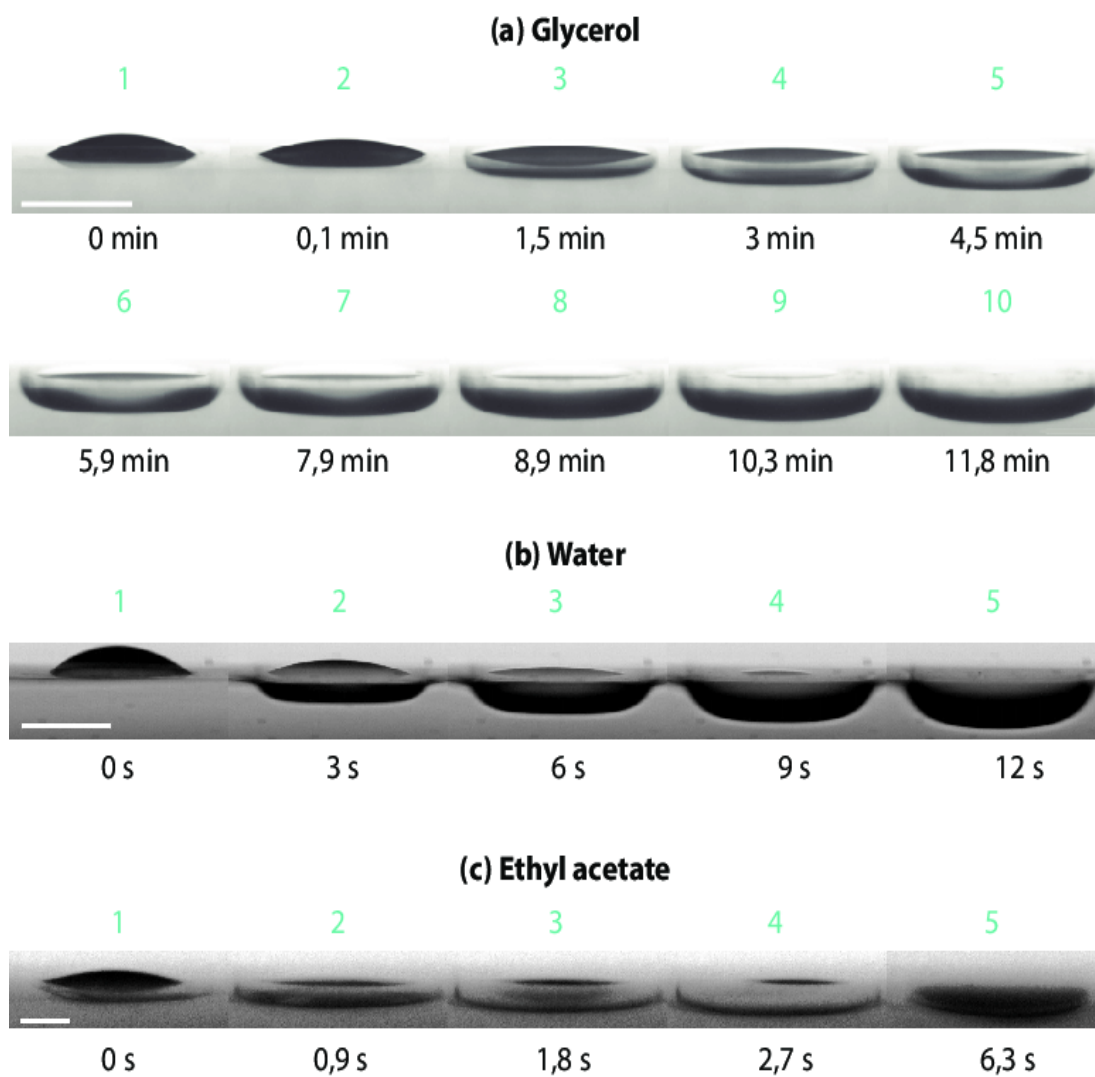


Figure 1.4: Side-view images of the evolution of the droplet and the wetting front for sessile (a) glycerol, (b) water, and (c) ethyl acetate droplets imbibing on a porous (colloidal silica) substrate. Reproduced from Figure 3 of Léang *et al.* [3] with permission, Copyright 2019, from the Royal Society of Chemistry.

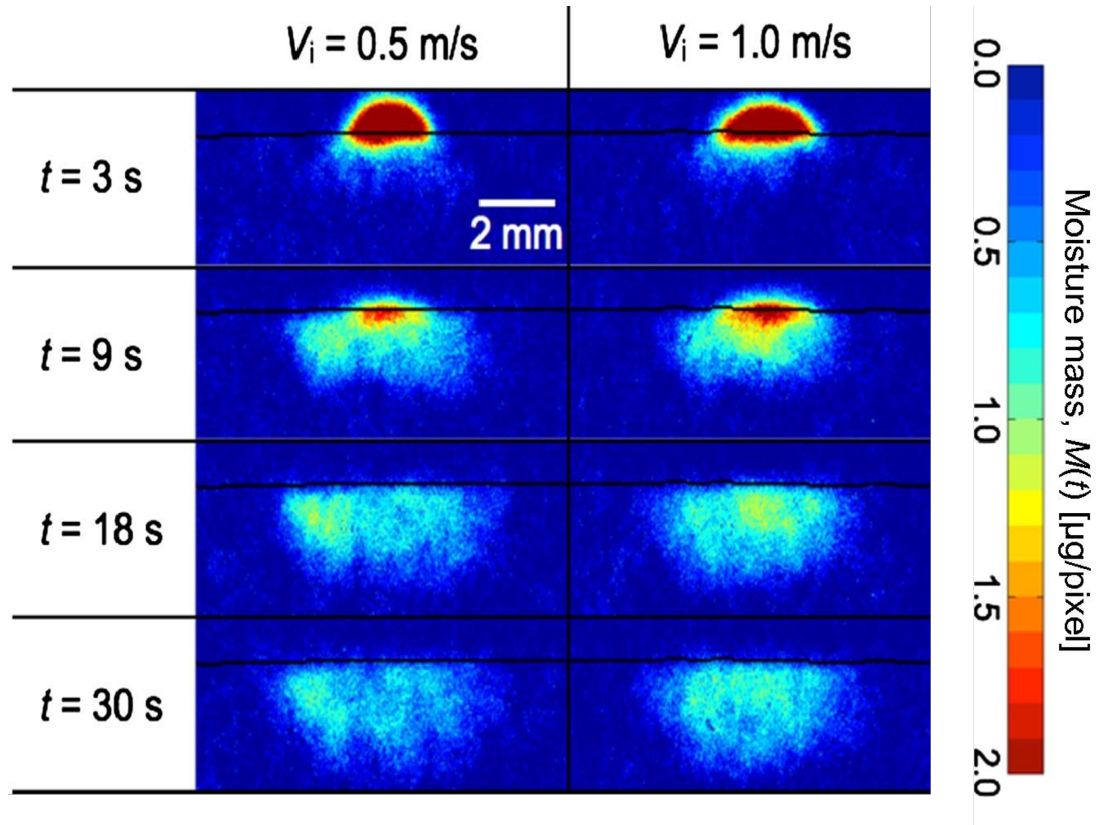


Figure 1.5: Side-view images of the evolution of the droplet and the wetting front for sessile water droplets imbibing on a porous (limestone) substrate, where V_i denotes the speed at which the droplet impacts the porous substrate. Reproduced from Figure 4 of Lee *et al.* [4] with permission, Copyright 2016, from Elsevier.

& Van Roost [44], Kumar & Deshpande [123], Daniel & Berg [19], Zdražil *et al.* [139], Nguyen *et al.* [140], Mendez *et al.* [141], Xiao *et al.* [142], Siregar *et al.* [143], Oko *et al.* [144], Lee *et al.* [4], Bhattacharjee *et al.* [145], Krainer & Ulrich [146,147], Léang *et al.* [3], Chebbi [148], van Gaalen *et al.* [149], Tan [124], Schlachter *et al.* [150], Waldner & Hirn [151], and Song *et al.* [152] have built on the works of Marmur [116,117] and Denesuk *et al.* [118] and have obtained exact, asymptotic, approximate and/or numerical descriptions of the evolution, and hence the lifetime, of a droplet undergoing imbibition on an initially dry porous substrate in a variety of situations. Notably, Clarke *et al.* [130] experimentally and theoretically investigated the simultaneous spreading and imbibition of an ink droplet on a finitely thick, anisotropic, initially dry, porous substrate. The authors described the evolution of a droplet by coupling a molecular-kinetic theory model for spreading with Darcy’s law for imbibition, and fitted numerical simulation data to experimental results to determine the physical properties that characterise mass transport into the substrate. In related work, Anderson [138] theoretically investigated the imbibition of a droplet on a deformable, finitely thick, anisotropic, initially dry, porous substrate, and extended the models developed by Denesuk *et al.* [118], Davis & Hocking [36], and Clarke *et al.* [130]. The imbibition was described using Darcy’s law, and the substrate was modelled as an elastic porous substrate in which the matrix deforms in response to imbibition. The author determined similarity solutions and developed numerical simulations to describe the evolution of droplets with pinned and unpinned contact lines. The author also demonstrated that pinning strongly influences both the final substrate shape and the evolution of the wetting front. In particular, unpinned contact lines reduce the contact area over time, which in turn slows imbibition and alters the slope of the final substrate shape, which can range from a raised mound to a depressed pit, with either smooth or sharp transitions. Additionally, Zdražil *et al.* [139] experimentally and theoretically investigated the simultaneous spreading, imbibition, and solidification of a hot, sessile (polyethylene glycol) droplet on a thick, anisotropic, initially dry, cooler, porous (sodium carbonate) substrate. The authors described the droplet and wetting front evolution in the presence of intermolecular forces, a precursor layer, and disjoining pressure, which they validated through com-

parison with experimental measurements. By fitting numerical simulations to measured droplet radius evolution, they identified key physical parameters governing mass transport into the substrate and phase change, and concluded that the relative timescales of spreading, imbibition, and solidification determine the shape of the solidified remnant of the original liquid droplet.

A number of experimental and theoretical investigations into the imbibition of droplets on porous substrates have modelled the transport of liquid from the base of the droplet into the pores as unsteady Fickian diffusion in which the imbibition is driven by the difference in the concentration of liquid between the surface of the substrate and the pores (see, for example, Oliver [153], Yip *et al.* [129], Desie & Van Roost [44], Willis *et al.* [10], Boulogne *et al.* [154,155], Richards *et al.* [11], and Duprat *et al.* [156]). The classic reference for concentration-driven imbibition is the treatment by Crank [157], which describes the theory and applications of transport by unsteady Fickian diffusion for a wide range of materials. Such models have been used to describe the imbibition of droplets on porous substrates which are able to swell; an example of this type of porous substrate is hydrogels, (see, for example, Boulogne *et al.* [154,155] and Duprat *et al.* [156]) or substrates which are treated with a surface coating which is less porous than that of the underlying substrate (see, for example, Yip *et al.* [129] and Desie & Van Roost [44]). We note that, due to its mathematical equivalence with the Darcy imbibition model into a finitely thick, anisotropic, initially dry, porous substrate (see, for example, Yip *et al.* [129]), the unsteady Fickian diffusion model for droplet imbibition is not treated explicitly in this thesis. Nevertheless, the results for the imbibition of a thin sessile droplet on a finitely thick, anisotropic, initially dry, porous substrate are formally equivalent to those that can be obtained from such a model.

The studies described in this section provide a comprehensive understanding of the imbibition of a sessile droplet on a porous substrate, establishing the physical mechanisms and modelling approaches relevant to flooded or initially dry porous substrates. In this thesis, imbibition is not treated in isolation, and instead, forms the second part of the simultaneous problem with evaporation, whose combined influence on droplet evolution, flow within the droplet, particle transport, and deposit formation is the cen-

tral focus of the work. Throughout this thesis, we consider Darcy-law-based models for flooded or initially dry porous substrates, although the lubrication-based framework developed in Section 2.4 can, in principle, also accommodate a variety of imbibition scenarios, including steady or unsteady Fickian diffusion.

1.6 Droplet Evaporation and Imbibition on a Porous Substrate

Having described the evaporation of a droplet on a solid substrate and the imbibition of a droplet on a porous substrate, in Sections 1.4 and 1.5, respectively, we now describe the situation in which both processes occur simultaneously (i.e., when an evaporating droplet also imbibes into a porous substrate). In this situation, mass is lost both to the atmosphere and the substrate. In this section, we describe the modelling approaches and key findings pertinent to the analysis undertaken within this thesis.

1.6.1 A Flooded Porous Substrate

Relatively few subsequent authors (with the exception of Pham & Kumar [109] and Hartmann & Thiele [158]) have built on the work of Davis & Hocking [35] to obtain exact, asymptotic, approximate, and/or numerical descriptions of the evolution of a droplet undergoing simultaneous evaporation and imbibition on a flooded porous substrate. Notably, Pham & Kumar [109] theoretically investigated the simultaneous spreading, evaporation, and imbibition of a particle-laden droplet on a finitely thick, anisotropic, flooded, porous substrate, in which flow occurred only in the vertical direction. In this work the evaporation was described using the one-sided model, rather than the diffusion-limited model, and the imbibition was described using Darcy’s law. Specifically, Pham & Kumar [109] described the evolution of, and deposition from, a droplet in the presence of intermolecular forces, a precursor layer, disjoining pressure, and surface roughness. Pham & Kumar [109] identified that evaporation and imbibition have qualitatively similar effects on the contact line dynamics of a droplet, and as a result, have qualitatively similar effects on particle deposition. Recently, Hartmann

& Thiele [158] investigated the simultaneous spreading, evaporation, imbibition, and condensation of a confined volatile droplet on a thin flooded porous substrate. Specifically, Hartmann & Thiele [158] described the evolution of a droplet using a thin-film approach based on a gradient dynamics formulation.

1.6.2 An Initially Dry Porous Substrate

In contrast to the investigation of the evolution of a droplet undergoing simultaneous evaporation and imbibition on a flooded porous substrate, many authors such as Willis *et al.* [10], Christodoulou *et al.* [159], Richards *et al.* [11], and Waldner *et al.* [160] have built on the work of Marmur [116,117] and Denesuk *et al.* [118] to obtain exact, asymptotic, approximate, and/or numerical descriptions of the evolution of a droplet undergoing simultaneous evaporation and imbibition on an initially dry porous substrate. Notably, Willis *et al.* [10] investigated, in the context of substrate contamination by a chemical warfare agent, the simultaneous evaporation and imbibition of a thin sessile droplet on military-relevant substrates. The evaporation and imbibition were described using unsteady Fickian diffusion models. Specifically, in the work of Willis *et al.* [10], the evolution of a thin sessile droplet was determined using finite element methods, and the numerical simulation data was fitted to experimental results to determine the mass loss into the atmosphere and substrate. In a related study, Richards *et al.* [11] investigated the simultaneous evaporation and imbibition of a thin sessile droplet on protective barrier substrates (such as gloves, face masks, or military uniforms). The evaporation was described using the diffusion-limited evaporation model and the imbibition was described using an unsteady Fickian diffusion model. Specifically, Richards *et al.* [11] described the evolution of the droplet and numerical simulation data was fitted to experimental data, in order to determine the mass transport into the atmosphere and substrate. We note that while Willis *et al.* [10] and Richards *et al.* [11] also considered the imbibition to be driven by concentration gradients within the substrate, in Section 3.3 we compare the model for droplet imbibition on a finitely thick, anisotropic, initially dry, porous substrate, developed in Section 2.7.1, with these authors' experimental results.

Following this, Christodoulou *et al.* [159] investigated, in the context of pharmaceutical tablet coating, the simultaneous spreading, evaporation, and imbibition of a thin sessile droplet on porous pharmaceutical tablet substrates. In this work the evaporation was described using the diffusion-limited evaporation model and the imbibition was described using Darcy’s law. Specifically, Christodoulou *et al.* [159] described the evolution of the droplet and wetting front in the presence of intermolecular forces, a precursor layer, and disjoining pressure. More recently, Waldner *et al.* [160] investigated, in the context of inkjet printing, the simultaneous spreading, evaporation, and imbibition of a thin sessile droplet on porous paper substrates. In this work a data-driven empirical model was used to describe evaporation and imbibition. Specifically, Waldner *et al.* [160] described the evolution of the droplet and wetting front in the presence of surface roughness.

Previous investigations of simultaneous evaporation and imbibition have been almost exclusively numerical, providing valuable qualitative and quantitative insight into droplet evolution on porous substrates but without yielding closed-form analytical results. In this thesis, we present, to the best of our knowledge, the first analytical analysis for the evolution of the droplet, flow within the droplet and substrate, and particle transport. Throughout this thesis, we consider flooded or initially dry porous substrates, using a lubrication-based approach that can accommodate a range of evaporation and imbibition models.

1.7 The Coffee-Ring Effect

In a wide variety of practical applications, the spatial distribution of the final deposit pattern left behind on the substrate once the droplet has entirely evaporated and/or imbibed is of considerable importance. For instance, in practical applications concerning droplets in ink-jet printing (see, for example He & Derby [161]) and DNA chip manufacturing (see, for example, Dugas *et al.* [162]) the desired outcome is usually a uniform deposit. In contrast, in practical applications concerning droplets in disease diagnostics (see, for example, Carreón *et al.* [163]) and conductive coatings (see, for

example, Layani *et al.* [164]) the desired outcome is usually either a single ring deposit or multiple ring deposits. Hence, a wide variety of practical applications would benefit from an improved ability to predict and/or control the final deposit pattern of a droplet undergoing simultaneous evaporation and imbibition *a priori* (see, for example, the review articles by Larson [51], Sefiane [165], Mampallil & Eral [166], Parsa *et al.* [167], Lohse [168], and Thampi & Basavaraj [169]).

The experimental and theoretical studies by Deegan *et al.* [52, 53] and Deegan [54] are credited with providing the first detailed explanation of the coffee-ring effect, in which a ring-shaped deposit is left behind at the position of the contact line when a particle-laden droplet with a pinned contact line evaporates. Deegan *et al.* [52, 53] and Deegan [54] identified that as a droplet evaporates according to the diffusion-limited model an outward capillary flow carries the suspended particles towards the contact line, leading to the formation of a characteristic coffee-ring deposit. Many subsequent authors, such as Popov [64], Hu & Larson [8], Zheng *et al.* [65], Marín *et al.* [170, 171], Nguyen *et al.* [172], Siregar *et al.* [143], Wray *et al.* [70–72], Freed-Brown [66, 173], Man & Doi [174], Zigelman & Manor [175, 176], Pham & Kumar [108], Yang *et al.* [177], Moore *et al.* [73, 74], van Gaalen *et al.* [149, 178, 179], Matavž *et al.* [180], Schumacher *et al.* [181], Coombs *et al.* [182, 183], D’Ambrosio *et al.* [82–84], and Moore *et al.* [184] have built on the work of Deegan *et al.* [52, 53] and Deegan [54] to investigate the final deposit pattern formed when a particle-laden droplet on a solid substrate undergoes evaporation.

The solutions for the flow within a thin sessile droplet evaporating with a pinned contact line according to the diffusion-limited evaporation model were given by Hu & Larson [59], Larson [51], Boulogne *et al.* [79], Wilson & D’Ambrosio [17], and D’Ambrosio *et al.* [84] while those for the spatially uniform variant of the diffusion-limited model were given by Boulogne *et al.* [79]. The solutions for the flow within a pinned, thin sessile droplet evaporating according to one-parameter family of local evaporative fluxes, which incorporates both the diffusion-limited model and spatially uniform variant were given by D’Ambrosio *et al.* [82].

The solutions for the mass of particles leaving the bulk of the droplet and be-

ing transferred to a ring deposit for a droplet evaporating according to the diffusion-limited model were given by Deegan *et al.* [53], Boulogne *et al.* [79], and Wilson & D’Ambrosio [17]. The mathematical model developed by Deegan *et al.* [53] predicts that all of the particles within a pinned evaporating particle-laden droplet are transported into a ring deposit of infinitesimal width. While this model captures the underlying physics of capillary-driven transport, the resulting (singular) deposit profile at the contact line is idealised and subsequent extensions have introduced additional physical mechanisms (such as particle jamming, diffusion, and substrate interaction) that yield better qualitative and quantitative agreement with experimentally observed ring deposit profiles. In particular, González-Gutiérrez *et al.* [5] experimentally investigated the final deposit pattern of a watercolour paint droplet evaporating and imbibing on a porous (paper) substrate and observed a ring deposit of finite width, as shown in Figure 1.6. In Figure 1.6 the Beer–Lambert law was used to determine the intensity of pixels across the surface of the substrate, which is related to the density of particles at each spatial location (see, for example, Wray *et al.* [72]).

Notably, Popov [64] extended the classical coffee-ring model to quantify the width and height of the ring deposit by introducing a jammed region, in which the particle concentration remains constant upon reaching the maximum packing fraction. This extension yields a finite-width deposit, the outer boundary of which is fixed at the contact line and the inner boundary of which advances inward as the droplet evaporates. Zheng [65] extended the work of Popov [64] by introducing a jammed region that conforms to the evolving shape of the droplet as it evaporates, allowing the particle concentration within the growing ring deposit to vary in both space and time. Kaplan & Mahadevan [185] extended prior work on the coffee-ring effect by allowing particles in the bulk of the droplet to be transported through a porous immobile matrix, resulting in a jammed region adjacent to the contact line.

Moore *et al.* [73, 74] investigated the early-stage formation of “nascent” coffee rings in thin sessile pinned evaporating droplets at large solutal Péclet number, before particle jamming occurs. In particular, the authors used matched asymptotic expansions and numerical simulations to resolve a narrow boundary layer near the contact line, in

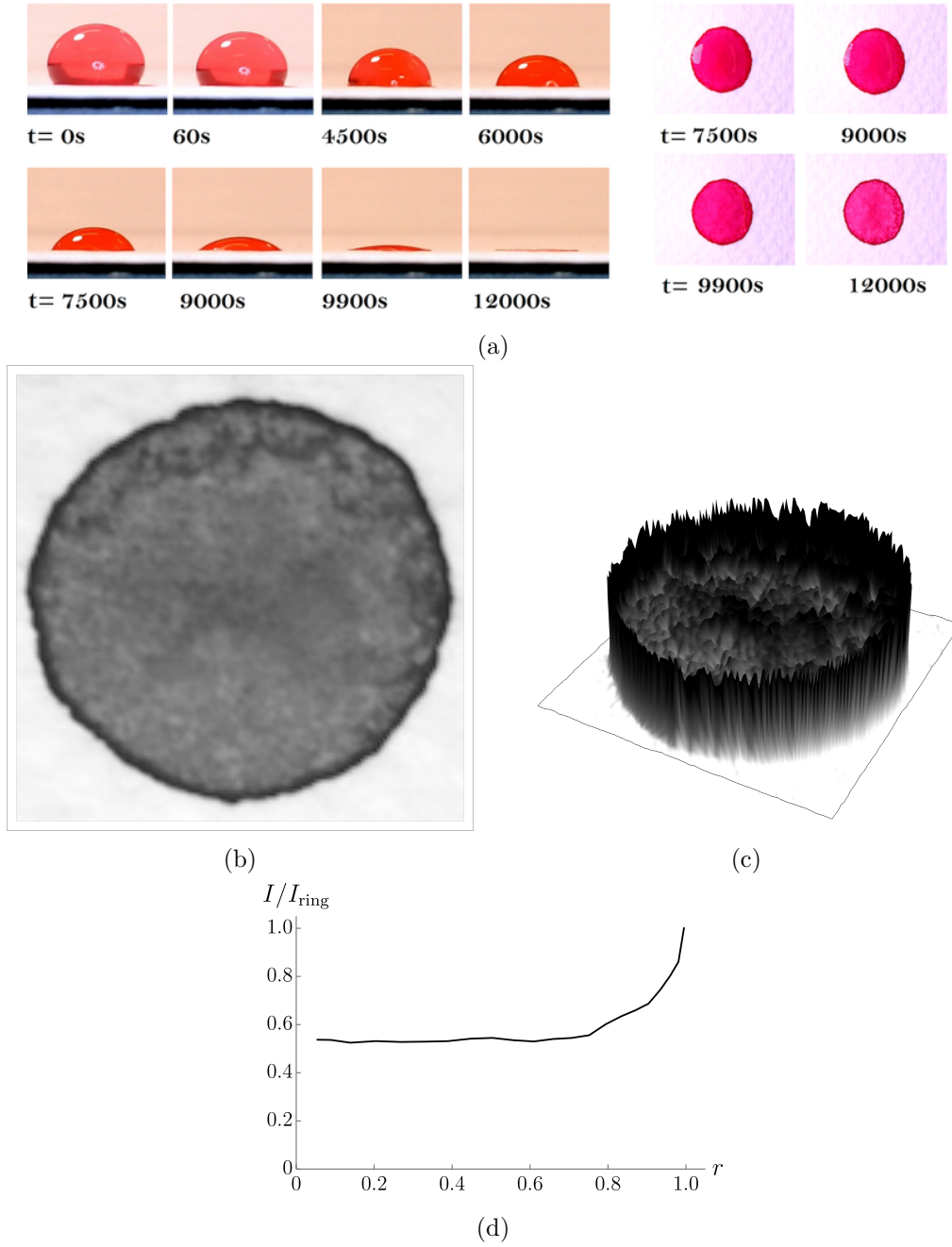


Figure 1.6: Images of the (a) side-view and top-view of the evolution of the droplet and (b) greyscale image of final deposit pattern at $t = 1200 s$ from Gutiérrez *et al.* [5]. Adapted from Figure 2 of Gutiérrez *et al.* [5], with permission from Professor Roberto Zenit. Plots of (c) pixel intensity of the final deposit pattern and (d) the average pixel intensity per radial bin (20 bins), where r is the radial coordinate and I and I_{ring} are the intensity within each radial bin and within the ring, respectively.

which diffusion counteracts the outward capillary flow. The authors showed that the assumption that diffusive effects can be ignored is invalid within this boundary layer. More recently, Moore & Wray [86] investigated the impact of gravitational effects on particle transport within evaporating droplets and identified that gravitational effects can diminish the height of the ring deposit, shift its location inward, and, under certain conditions, generate a secondary interior peak in the concentration of particles within the droplet.

Dou *et al.* [186] and Dou & Derby [187] pioneered the experimental and theoretical investigation of the formation of a coffee-ring deposit when a droplet imbibes into a porous substrate. Dou & Derby [187] identified that (in a similar manner to diffusion-limited evaporation) as a droplet imbibes an outward capillary flow carries the suspended particles towards the contact line, leading to the formation of a coffee-ring deposit. Several subsequent authors, such as Boulogne *et al.* [154, 155], Al-Milaji *et al.* [188], and Hwang *et al.* [189] have built on the work of Dou *et al.* [186] and Dou & Derby [187] to investigate the final deposit pattern formed when a particle-laden droplet on a porous substrate undergoes imbibition. Likewise, several authors such as Pack *et al.* [1], Pham & Kumar [109], González-Gutiérrez *et al.* [5], Li *et al.* [6], Kumar *et al.* [190], Wijburg *et al.* [191], Wang & Darhuber [192], and Niu *et al.* [193] have investigated the final deposit pattern formed when a particle-laden droplet undergoes simultaneous evaporation and imbibition.

Throughout this thesis we assume that the suspended particles within the droplet are larger than the characteristic pore size and therefore cannot penetrate the substrate. Table 1.1 provides order-of-magnitude estimates of the reduced Péclet number, as discussed in Section 2.8, for representative particle sizes relevant to small ions/molecules, small proteins, gold nanoparticles, polystyrene, silical microspheres, and colloids suspended in a water droplet at 298 K. The particle size and diffusivity estimates in Table 1.1 are taken from Holz *et al.* [194], Tyn & Gusek [195], Ullman *et al.* [196], Stöber *et al.* [197], Turkevich *et al.* [198], Cho *et al.* [199]). In the absence of reported particle diffusivities, the values are estimated using the Stokes-Einstein law (see, for example, Miller [200]). These values show that Pe^* spans several orders of magnitude across

the particle sizes considered, indicating the parameter ranges over which our models remain valid. Provided that the characteristic particle size exceeds the pore size of the substrate, the particles cannot penetrate the substrate, and the modelling assumptions underlying the two transport regimes discussed in Section 2.8 remain valid.

Particle Type	Size	D_p (m ² /s)	Pe*	Pe*
			($t_{\text{ref}} = 10^1$ s)	($t_{\text{ref}} = 10^5$ s)
Small ions/molecules	0.2–0.3 nm	1×10^{-9}	25	2.5×10^{-3}
Small proteins	4–7 nm	1×10^{-10}	250	2.5×10^{-2}
Gold nanoparticles	10–50 nm	$1\text{--}5 \times 10^{-11}$	500–2500	$5 \times 10^{-2}\text{--}2.5 \times 10^{-1}$
Polystyrene	100 nm	5×10^{-12}	5000	5×10^{-1}
Silica microspheres	1 μm	5×10^{-13}	5×10^4	5
Colloids	2–5 μm	1×10^{-13}	2.5×10^5	25

Table 1.1: Order of magnitude estimates of the reduced Péclet number $\text{Pe}^* = \theta_0^2 R_0^2 / (D_p t_{\text{ref}})$ for representative particle sizes, using $R_0 = 10^{-3}$ m, $\theta_0 = 0.5$ radians, and $t_{\text{ref}} = 10^1\text{--}10^5$ s for a water droplet at 298 K.

1.8 Suppressing the Coffee-Ring Effect

Suppression of the coffee-ring effect when a droplet evaporates and/or imbibes with a pinned contact line can be achieved through strategies that either suppress the outward capillary flow or immobilise particles before they can reach the ring deposit. Numerous approaches have been reported in the literature, and in this subsection we focus on those most pertinent to the objectives of this thesis. As a basis for this discussion, and given the diverse range of deposit patterns identified through experimental and/or theoretical studies of droplet evaporation and/or imbibition, Figure 1.7 illustrates the various final deposit patterns reported in the literature and discussed throughout this thesis, along with the terminology used to describe them.

1.8.1 Porous Substrates

While Dou *et al.* [186], Dou & Derby [187], and Boulogne *et al.* [154] identified that the coffee-ring effect is present in a droplet undergoing imbibition, there are investigations within the literature which show that, in instances in which particles are able

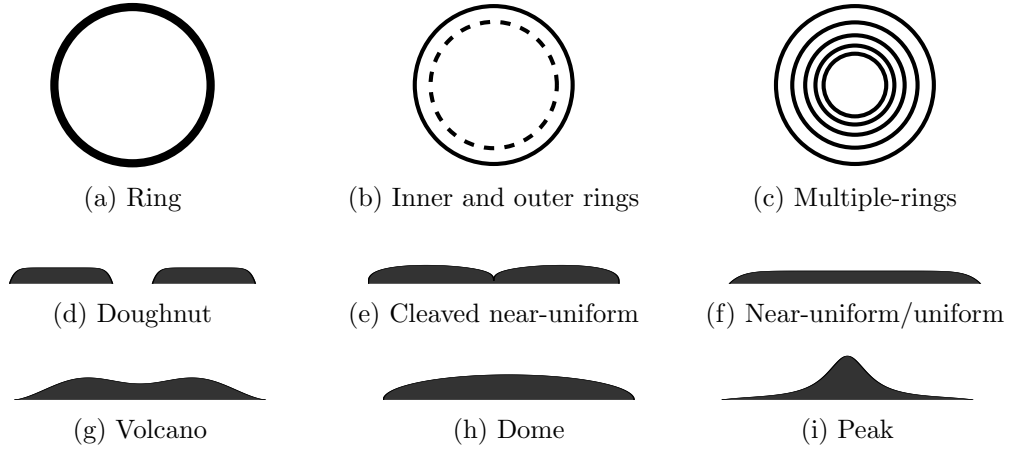


Figure 1.7: Sketches of various final deposits experimentally and theoretically investigated within the current literature on droplet evaporation and imbibition, and discussed throughout this thesis.

to be transported into the pores (i.e., when the average particle size is smaller than the average pore size), the final ring deposit is less pronounced. In particular, Pack *et al.* [1] experimentally investigated the final deposit pattern of nanoparticle-laden droplets evaporating and imbibing on nanoporous (aluminium oxide and glass) substrates and found that, while the deposit pattern was concentrated near the droplet edge, in situations where the average pore size exceeded the particle diameter the ring deposit was less pronounced, as particles were transported into the pores of the substrate during imbibition. Similarly, Li *et al.* [6] experimentally investigated the final deposit pattern of particle-laden droplets evaporating and imbibing on nanoporous substrates and found that, while the deposit pattern was concentrated near the droplet edge, an additional outer ring formed within the substrate when particles were transported into the pores during droplet imbibition, as shown in Figure 1.8.

1.8.2 Contact-line De-pinning

The formation of a ring deposit, as discussed in Section 1.7, requires a pinned contact line. Hence, the most simple and effective way to suppress the coffee-ring effect is through conditions that result in the contact line de-pinning during droplet evolution. The final deposit pattern formed on the surface of the substrate when a droplet

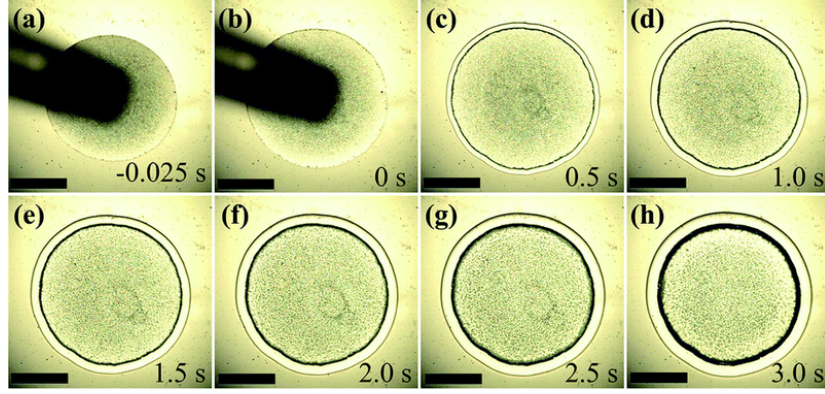


Figure 1.8: Images of the evolution of the ring deposits formed at the contact line and within the substrate. The images show a particle-laden droplet undergoing simultaneous evaporation and imbibition, with an initial volume of 0.5 mm^3 and initial particle concentration of 1 wt %. The scale bars represent a distance of 0.8 mm. Adapted from Figure 3 of Li *et al.* [6] with permission, Copyright 2020, from the Royal Society of Chemistry.

evaporates and/or imbibes with an unpinned contact line has been studied theoretically and/or experimentally (see, for example, Fukai *et al.* [201], Kaneda *et al.* [202], Kajiya *et al.* [203], Biswas *et al.* [204], Freed-Brown [66,173], Man & Doi [174], Patil *et al.* [205], Boulogne [154,155], Zigelman & Manor [175], Das *et al.* [206], Lee *et al.* [207], Thokchom *et al.* [208], Kim *et al.* [209], Pham & Kumar [109], Lee & Kim [210], Matavž *et al.* [180], Niu *et al.* [193], and D'Ambrosio *et al.* [84]).

The solutions for the flow within a thin sessile droplet evaporating in the CA mode according to the diffusion-limited evaporation model were given by Gelderblom *et al.* [16] and D'Ambrosio *et al.* [84], while those for spatially uniform evaporation were given by Freed-Brown [66]. Gelderblom *et al.* [16] identified that as a droplet evaporates according to the diffusion-limited model an outward capillary flow carries particles towards the unpinned contact line. We note that, although Gelderblom *et al.* [16] did not perform further analysis, as shown by D'Ambrosio *et al.* [84], in combination with the movement of the contact line, the outward capillary flow results in a cleaved near-uniform final deposit, in which the deposit profile is nearly uniform across the surface of the substrate, with a cleave at the centre of the deposit. In contrast, Freed-Brown [66] identified that as a droplet evaporates according to spatially uniform evaporation an

inward capillary flow carries particles towards the centre of the droplet. However, the contact line recedes faster than the speed at which the particles are advected by the flow, and, as a result, all particles are eventually captured by the receding contact line. Consequently, a peak deposit is formed on the surface of the substrate. Building on this, Freed-Brown [173] numerically simulated the deposit pattern from a droplet undergoing diffusion-limited evaporation on a solid substrate, and also showed that a cleaved near-uniform deposit is formed on the surface of the substrate.

Man & Doi [174], extending Freed-Brown’s work [66], investigated how contact-line friction and evaporation rate influence the deposition from a thin sessile droplet undergoing evaporation. The evaporation was described using a spatially uniform model. Man & Doi [174] identified transitions from ring to volcano to peak deposits, respectively. Zigelman & Manor [175] theoretically investigated the evolution of, flow within, and deposition from a droplet undergoing evaporation with pinned and unpinned contact lines. In this work the evaporation was described using the diffusion-limited evaporation model. The authors showed that, consistent with previous studies, evaporation in the CR and CA modes leads to the ring and volcano or peak deposit patterns. In contrast, evaporation in the SJ mode leads to multiple concentric ring deposits. In Section 2.8 we develop a model similar to that of Zigelman & Manor [175] to describe the final deposit pattern formed when a droplet undergoes simultaneous evaporation and imbibition in the CR, CA, SS, and SJ modes.

Thokchom *et al.* [208] experimentally investigated droplets evaporating on solid (glass) substrates and observed a transition from a ring deposit when the contact line was pinned to either a uniform or doughnut deposit when the contact line was unpinned. In particular, Thokchom *et al.* [208] identified that increasing the sugar concentration within an evaporating droplet promoted contact-line de-pinning, as shown in Figure 1.9. Shimobayashi *et al.* [7] experimentally investigated droplets evaporating on solid (ceramic) substrates and observed a transition from a ring deposit when the contact line was pinned to a volcano and dome deposits when the contact line was unpinned. Similarly, Matavž *et al.* [180] experimentally investigated ink droplets evaporating on solid (silicon wafer) substrates and observed a transition from a ring deposit when the contact

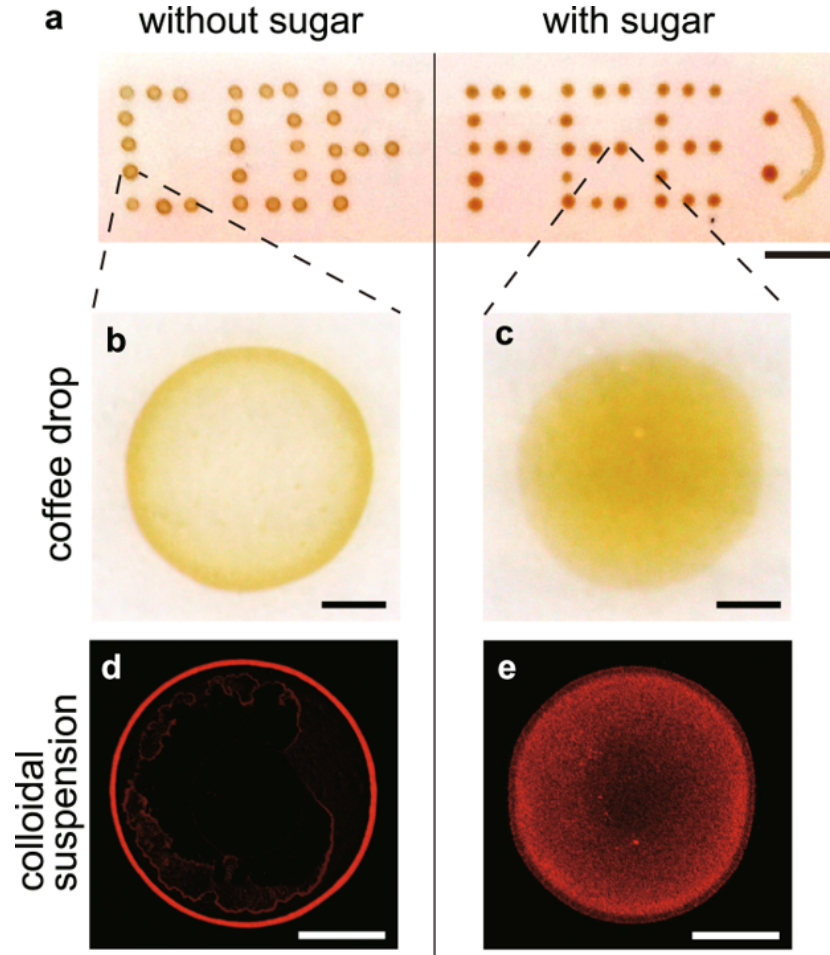


Figure 1.9: Final deposit patterns from pinned and unpinned evaporating droplets. (a) Bright field image of coffee-laden droplets without and with caster sugar (97.8 % sucrose) in 200 mM. The scale bar is 1 cm. (b,c) Enlarged images from (a) where a ring deposit and dome deposit are formed in (b) and (c), respectively. The scale bars are 500 μm . (d,e) Confocal images of the final deposit pattern of droplets (1 μm in diameter, 0.5 μl , and 0.1 vol %) without sugar and with sucrose (200 mM), where a ring deposit and doughnut deposit are formed in (d) and (e), respectively. The scale bars are 500 μm . Adapted from Figure 1 of Shimobayashi *et al.* [7] with permission, Copyright 2018, from Nature.

line was pinned to a dome deposit when it was unpinned. Boulogne [154, 155] experimentally investigated droplets imbibing on porous (hydrogel) substrates and observed a transition from a ring deposit when the contact line was pinned to a near-uniform deposit when it was unpinned. Niu *et al.* [193] experimentally investigated droplets evaporating and imbibing on nanoporous (paper) substrates and evaporating on solid (glass) substrates. They observed contact-line de-pinning in both cases, but found that the contact line receded more rapidly on porous substrates. In both cases, the final deposit was a near-uniform deposit.

D’Ambrosio *et al.* [84] theoretically investigated droplets evaporating in the CR, CA, SS, and SJ modes. In this work the evaporation was described using the basic or spatially uniform diffusion-limited model. Specifically, the authors described the evolution of, flow within, and deposition from a thin sessile droplet. The authors determined analytical expressions for the evolution of the particle concentration within the droplet, the surface density of deposited particles on the surface of the substrate, and the mass of particles remaining in and leaving the droplet, respectively. The results were compared quantitatively with experimental measurements across a range of contact-line behaviours, with the model successfully reproducing both the qualitative deposit profile for unpinned contact lines and the quantitative mass distributions of multiple-ring deposits. Building on this work, we extend this analysis to droplets undergoing simultaneous evaporation and imbibition on the three different porous substrates discussed in Section 1.5.

1.8.3 Marangoni Flows

Marangoni flows are driven by surface-tension gradients that develop along the liquid–air interface of an evaporating droplet. In general, the surface tension depends on both the temperature and the chemical composition at the interface. Consequently, there are a variety of different types of Marangoni flows depending on the physical mechanism inducing the variation in the surface tension. Thermal Marangoni flow arises when temperature differences develop along the free surface, for example due to evaporative cooling or heating of the substrate. Solutal Marangoni flow results from

variations in the concentration of solutes or surfactants along the free surface. These two mechanisms can act simultaneously, either reinforcing or opposing one another, and their interplay can generate complex circulatory patterns that strongly influence particle deposition during evaporation and/or imbibition. These internal circulatory flows can be strong enough to compete with, or even overcome, the outward capillary flow that transports particles toward the contact line. Depending on their direction and strength, Marangoni flows can redistribute suspended particles away from the droplet edge and toward the centre, suppressing the coffee-ring effect, and/or create complex flow fields inside the droplet (see, for example, Hu & Larson [8,57–59], Sáenz *et al.* [211], Pham & Kumar [109], van Gaalen *et al.* [178,179,212], Williams *et al.* [213], and Rocha *et al.* [214]).

Notably, Hu & Larson [8] extended the basic diffusion-limited evaporation model to consider the additional effect of thermal Marangoni flows on the flow within an evaporating droplet. Experiments with particle-laden droplets validated the modelling prediction that sufficiently strong Marangoni flows can transport particles inward in a circulatory flow, suppressing ring deposit formation. Figure 1.10 shows the effect of thermal Marangoni on the flow-field within an evaporating octane droplet, as experimentally investigated by Hu & Larson [8]. While Hu & Larson [8] focused on solid substrates, Dou *et al.* [186] and Dou & Derby [187] investigated the effect of solutal Marangoni flows on ink droplets undergoing simultaneous evaporation and imbibition. For droplets evaporating on a solid substrate, a volcano deposit formed due to solutal Marangoni flows overcoming the outward capillary flow, concentrating particles toward the droplet centre. In contrast, for droplets evaporating and imbibing on a porous (powder-bed) substrate, a ring deposit formed as the additional outward flow due to imbibition overwhelmed the inward Marangoni flow, concentrating particles near the contact line.

1.8.4 Particle Interactions

In Sections 1.8.1–1.8.3 we have described methods to suppress the coffee-ring effect by altering the outward capillary flow. However, the final deposit pattern will be deter-

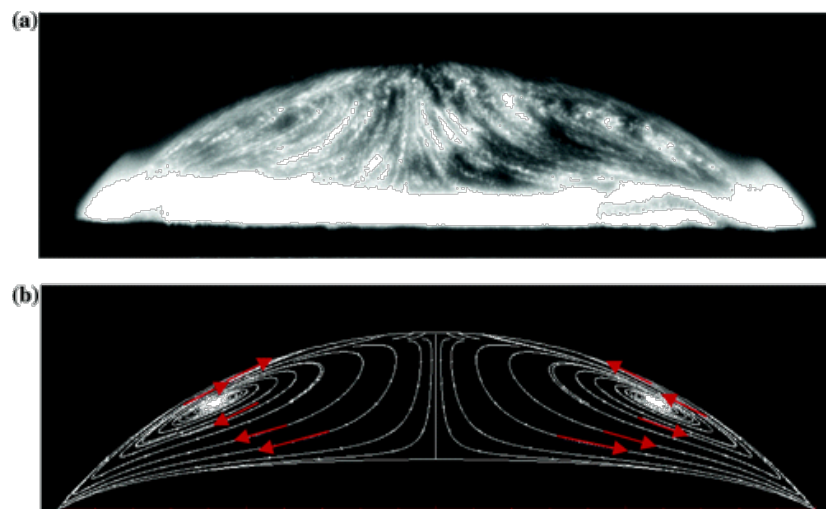


Figure 1.10: Images showing the effect of thermal Marangoni on the flow-field within an evaporating octane droplet, as experimentally investigated by Hu & Larson [8]. Reproduced with permission, Copyright 2006, from The Journal of Physical Chemistry B.

mined by a combination of both the capillary flow and particle interactions. Specifically, particle interactions can be decomposed into particle–substrate, particle–particle, and particle–free-surface interactions.

Particle–substrate interactions can suppress the coffee-ring effect by anchoring suspended particles to the surface of the substrate before the outward capillary flow can transport them to the contact line. When the substrate surface is chemically or physically modified to promote strong particle adhesion (e.g., through covalent bonding, electrostatic attraction, hydrogen bonding, or van der Waals forces) particles become adsorbed at their initial point of contact with the surface of the substrate. Particle–particle interactions can suppress the coffee-ring effect by aggregating suspended particles before the outward capillary flow can transport them to the contact line. When the particles within the droplet promote strong cohesion (e.g., through electrostatic forces, or capillary bridging) particles form clusters which may then disrupt the flow or sediment onto the surface of the substrate. Particle–free-surface interactions can suppress the coffee-ring effect by trapping suspended particles at the liquid–air interface before the outward capillary flow can transport them to the contact line. When the interface is chemically or physically modified to promote strong particle attachment

(e.g., through particle self-assembly, jamming, Marangoni flows, or surfactant-mediated interactions) particles may alter the shape of the free surface or drive inward flow away from the contact line. Several authors such as Widjaja & Harris [215], Yunker *et al.* [9], Siregar [216], Siregar *et al.* [143], Crivoi & Duan [217], Crivoi *et al.* [218], Zigelman & Manor [176], Kumar & Pham [108], Ren *et al.* [219], van Gaalen *et al.* [212], Erdem *et al.* [91], and D’Ambrosio *et al.* [83] have investigated the impact of particle interactions on the final deposit pattern formed from an evaporating and/or imbibing droplet.

Notably, Widjaja & Harris [215] theoretically investigated the final deposit pattern from a pinned droplet undergoing evaporation. The evaporation was described by the diffusion-limited model. The authors identified a range of final deposit patterns, from ring to nearly-uniform deposits. The final deposit pattern was governed by the balance between particle advection, diffusion, and adsorption. Sung *et al.* [220] theoretically investigated the same situation as Widjaja & Harris [215] with the additional effect of the desorption of particles from the substrate. Siregar [216] theoretically investigated the evolution of, and deposition from, both pinned and unpinned evaporating or imbibing particle-laden droplets in the presence of intermolecular forces, a precursor layer, disjoining pressure, and particle–substrate adsorption and desorption. Although evaporation and imbibition were not modelled simultaneously, the author identified that evaporation and imbibition have similar effects on contact-line dynamics, and hence, particle deposition. For imbibition on an initially dry porous substrate, varying substrate thickness, permeability, and capillary pressure showed that adsorption within the pores was greatest near the surface and decreased toward the wetting front. Building on this, Siregar *et al.* [143] investigated evaporating particle-laden droplets and quantified the influence of contact-line dynamics on both the spatial distribution and total mass of particles adsorbed to the substrate. In the physical system examined, pinned contact lines produced edge-concentrated deposits, whereas unpinned contact lines yielded peak deposits, and pinning led to a greater total adsorbed mass of particles on the surface of the substrate.

Van Gaalen *et al.* [212] theoretically investigated the de-pinning mechanisms of evaporating droplets with the incorporation of both insoluble and soluble surfactants

at the free surface. Specifically, van Gaalen *et al.* [212], in order to incorporate moving contact lines, implemented a precursor film or a slip length model. When compared with the experimental data of Nguyen *et al.* [172], the numerical results showed closer agreement with the slip-length model than with the precursor-film model. Van Gaalen *et al.* [149] theoretically investigated both pinned and unpinned droplets imbibing into an initially dry porous substrate in the presence of particle–substrate adsorption. In this work the imbibition was described using Darcy’s law. Specifically, van Gaalen *et al.* [149] described the evolution of a droplet, and wetting front, in the presence of intermolecular forces, a precursor layer, disjoining pressure, slip, and particle–substrate adsorption. Van Gaalen *et al.* [149] identified that a pinned contact line results in a mostly flat, radially expanding wetting front, while an unpinned contact line produces a parabolic wetting front which imbibes further into the substrate. In the presence of particle–substrate adsorption, the rate of imbibition increases if the timescale for particle–substrate adsorption is slow relative to that for imbibition, enabling surfactant to reach and adsorb at the wetting front. In contrast, if the timescale for particle–substrate adsorption is fast relative to that for imbibition, surfactant is unable to reach the wetting front, and instead adsorbs on the pore walls.

Yunker *et al.* [9] experimentally investigated the effect of particle shape on the final deposit pattern from an evaporating droplet. Specifically, Yunker *et al.* [9] identified that spherical (polystyrene) particles form a ring deposit, whereas ellipsoidal (polystyrene) particles deform the free surface and induce strong, long-range particle–particle attractive interactions that assemble loosely packed or arrested clusters, leading to the formation of a uniform deposit, as shown in Figure 1.11. Crivoi & Duan [217], Crivoi *et al.* [218], and Ren *et al.* [219] employed Monte Carlo simulations to investigate the transition from ring to uniform deposits formed on the surface of the substrate when a droplet evaporates with a pinned contact line. According to the model of Crivoi & Duan [217], suppression of the coffee-ring effect at the contact line requires the simultaneous presence of particle adsorption at the free surface, long-range particle–particle attractive interactions, and Marangoni flows. The required interplay of mechanisms highlights the relative strength of the outward capillary flow to trans-

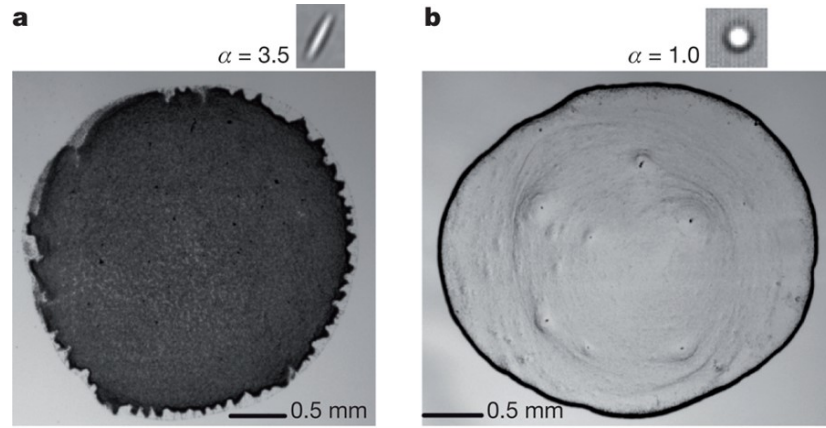


Figure 1.11: Images of the final deposit profile from an evaporating water droplet laden with polystyrene particles showing that (a) ellipsoidal particles form a near-uniform deposit and (b) spherical particles form a ring deposit. Adapted from Figure 1 of Yunker *et al.* [9] with permission, Copyright 2011, from Springer Nature.

port particles to the edge of a droplet and the conditions required to counteract such flow.

Zigelman & Manor [176] theoretically investigated the effect of particle–substrate adsorption and particle–particle coagulation on the final deposit pattern formed when a thin sessile pinned droplet undergoes evaporation. The evaporation was described by spatially uniform evaporation. In particular, Zigelman & Manor [176] identified a critical value of particle–substrate adsorption at which a uniform deposit forms. They further observed a transition from a ring deposit, below this value, to a peak deposit above it. Erdem *et al.* [91] theoretically investigated the evolution of, and deposition from, a thin two-dimensional droplet undergoing one-sided evaporation. In particular, the authors analysed the impact of contact-line motion, Marangoni flows, particle–substrate adsorption, and particle diffusion on the final deposit pattern. In particular, the authors recovered several of the deposit patterns investigated by previous authors, namely ring, near-uniform, volcano, dome, and peak deposits. D’Ambrosio *et al.* [83] theoretically investigated the adsorption of particles onto the substrate surface of an evaporating droplet with a pinned contact line. The droplet evaporation was described by the diffusion-limited model or a spatially uniform variant. In particular, D’Ambrosio *et al.* [83] identified that the presence of particle–substrate adsorption

completely suppresses the formation of a ring deposit when the evaporation is spatially uniform, but only partially suppresses the formation of a ring deposit when the evaporation is diffusion-limited. However, in both cases, the final adsorbed deposit is concentrated near the contact line when radial advection dominates particle–substrate adsorption, and concentrated near the centre when particle–substrate adsorption dominates radial advection. Building on this, Moore *et al.* [184] theoretically investigated the effects of particle advection, particle diffusion, and particle–substrate adsorption on the early-time evolution of the ring deposit. In particular, the authors identified that the presence of particle–substrate adsorption suppresses particle transport into the boundary-layer region, and hence reduces the mass of particles transported to the nascent ring deposit at early times.

While strategies for suppressing the coffee-ring effect have been extensively studied for droplets undergoing either evaporation or imbibition in isolation, few theoretical investigations have investigated the simultaneous problem. In this thesis, we examine the effectiveness of porous substrates and contact-line de-pinning in suppressing the coffee-ring effect for droplets undergoing simultaneous evaporation and imbibition.

1.9 Thesis Outline

Motivated by the wide variety of practical applications that would benefit from theoretical insight into the evolution of a droplet on a porous substrate and the formation of various final deposit patterns, in this thesis, we investigate the evolution of, flow within, and deposition from, a droplet undergoing simultaneous evaporation and imbibition using a combination of analytical and numerical techniques.

In Chapter 2 we formulate a mathematical model for the evolution of a thin sessile droplet undergoing simultaneous evaporation and imbibition on a porous substrate. Specifically, we provide a detailed description of the evaporation and imbibition models considered throughout this thesis, namely diffusion-limited evaporation; flooded, isotropic and anisotropic imbibition; and initially dry, anisotropic imbibition. We then formulate the hydrodynamic problem and the particle transport and deposition problem. In Chapter 3 we analyse mathematical models for the evolution of a thin sessile

droplet in the three situations considered in this thesis. In Chapter 4 we analyse the flow within the droplet and substrate for the three situations considered in this thesis. In Chapter 5 we analyse the concentration of particles and mass of particles within, and leaving, the bulk of the droplet in the three situations considered in this thesis. In Chapter 6 we calculate the paths of particles within the droplet for the three situations considered in this thesis. In Chapter 7 we discuss the implications of the results obtained throughout this thesis, draw conclusions, and discuss open questions and possible directions for future work on a droplet undergoing simultaneous evaporation and imbibition on a porous substrate.

1.10 Publications and Presentations

Several aspects of the investigation of a thin sessile droplet undergoing simultaneous evaporation and imbibition on a flooded, isotropic porous substrate have been presented at several local and international conferences, namely the British Applied Mathematics Colloquium, Newcastle University, Newcastle in April 2024; 10th International Bifurcations and Instabilities in Fluid Dynamics, University of Edinburgh, Edinburgh in June 2024; and the 1st European Fluid Dynamics Conference, RWTH Aachen University, Aachen, in September 2024. In addition, aspects of this investigation were presented in poster form at the 37th Scottish Fluid Mechanics Meeting, University of Edinburgh, Edinburgh in May 2024. An account of this work has recently been published in *Physical Review Fluids* (Craig *et al.* [221]).

Several aspects of the investigation of a thin sessile droplet undergoing simultaneous evaporation and imbibition on an initially dry, anisotropic porous substrate have been presented at several local and international conferences, special interest groups and research visits, namely at the UK Fluids Conference, University of Strathclyde, Glasgow in October 2023; Droplet Dynamics, University of Warwick, Coventry in June 2025; 6th International Conference on Droplets: Droplets 2025, University of Liège, Liège in July 2025; and Applied and Industrial Mathematics Research Group Seminar, University of Bath, Bath in December 2025. In addition, aspects of this work were presented in poster form at the 38th Scottish Fluid Mechanics Meeting, University of Glasgow, Glasgow in

Chapter 1. Introduction

May 2025. An account of this work is currently being prepared for publication.

Several aspects of the investigation of a thin sessile droplet undergoing simultaneous evaporation and imbibition on a flooded, anisotropic porous substrate has been presented orally by myself at several special interest groups and local conferences, namely at Droplet and Flow Interactions with Bio-inspired and Smart Surfaces, Durham University, Durham in November 2022, Droplet Dynamics, Wadham College, University of Oxford, Oxford in March 2023, British Applied Mathematics Colloquium, University of the West of England, Bristol in April 2023, and the 36th Scottish Fluid Mechanics Meeting, University of Strathclyde, Glasgow in May 2023. In addition, aspects of this investigation were presented in poster form by myself at an international summer school, namely The Power and Beauty of Asymptotic Methods, International Centre for Mechanical Sciences, Udine, Italy in June 2023.

Chapter 2

Mathematical Model of Droplet Evaporation and Imbibition

2.1 Overview

In this chapter, we develop mathematical models for a thin sessile droplet undergoing simultaneous evaporation and imbibition on the three porous substrates discussed in Section 1.3.

In Section 2.2 we formulate the general problem set-up, coordinate system and key variables which we will consider throughout thesis. In Sections 2.3 and 2.4 we formulate the hydrodynamic problem and describe the evolution of, and flow within, a thin droplet undergoing simultaneous evaporation and imbibition. In Section 2.5 we describe the modes of evolution which we will consider. In Section 2.6 we describe the diffusion-limited evaporative problem. In Section 2.7 we describe the imbibition problems which we will consider. In Section 2.8 we describe the particle transport and deposition problem.

2.2 Droplet Wetting

After being deposited onto the surface of a substrate, a thin sessile droplet undergoes a relatively short initial period during which it rapidly adjusts to its quasi-static shape

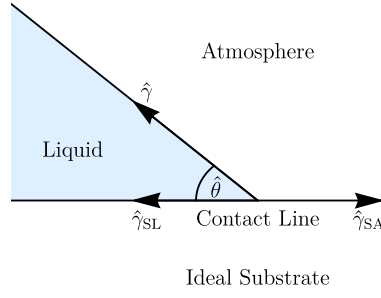


Figure 2.1: Sketch of the three-phase boundary between the substrate, atmosphere, and free surface of the droplet (i.e., the contact line) for a thin sessile droplet situated on the hydrophilic surface of an ideal solid or porous substrate.

defined by the initial value of the equilibrium contact angle, denoted by $\hat{\theta}_0$. The initial value of the contact radius is denoted by $\hat{R}_0$. The Young–Dupré equation,

$$\hat{\gamma} \cos \hat{\theta}_0 = \hat{\gamma}_{SA} - \hat{\gamma}_{SL}, \quad (2.1)$$

describes the equilibrium contact angle of a sessile droplet on an ideal (i.e., smooth and chemically homogeneous) substrate, where $\hat{\gamma}$, $\hat{\gamma}_{SA}$, and $\hat{\gamma}_{SL}$ denote the constant coefficient of surface tension at the droplet-atmosphere interface, substrate-atmosphere interface, and droplet-substrate interface, respectively. The extent of wetting is characterised by the value of $\hat{\theta}_0$. Throughout this thesis we investigate sessile droplets which have a high degree of wetting, corresponding to values of $\hat{\theta}_0$ in the range $0 < \hat{\theta}_0 < \pi/2$ (i.e., the substrate is “hydrophilic”). Figure 2.1 shows a sketch of the three-phase boundary between the substrate, atmosphere, and free surface of the droplet (i.e., the contact line) for a thin sessile droplet situated on the hydrophilic surface of an ideal solid or porous substrate.. We note that the uniqueness of the contact angle of a sessile droplet on an ideal substrate, as described by equation (2.1), is not the case in reality, as substrates are non-ideal and there is often a range of equilibrium contact angles (see, for example, De Gennes *et al.* [222]). The difference between the largest and smallest measurable equilibrium contact angles is known as “contact-angle hysteresis”.

2.3 Problem Formulation

We refer the description to polar coordinates $\hat{r}$ and $\hat{z}$ with $O\hat{z}$ perpendicular to the surface of the substrate at $\hat{z} = 0$. We denote the free surface of the droplet by $\hat{z} = \hat{h}(\hat{r}, \hat{t})$, the radial and axial components of the velocity within the droplet by $\hat{u} = \hat{u}(\hat{r}, \hat{z}, \hat{t})$ and $\hat{w} = \hat{w}(\hat{r}, \hat{z}, \hat{t})$, respectively, and the pressure within the droplet by $\hat{p} = \hat{p}(\hat{r}, \hat{z}, \hat{t})$, where $\hat{t}$ denotes time. The local evaporation and imbibition mass fluxes are denoted by $\hat{J}_E = \hat{J}_E(\hat{r}, \hat{t})$ and $\hat{J}_I = \hat{J}_I(\hat{r}, \hat{t})$, and the corresponding global evaporation and imbibition mass fluxes are denoted by $\hat{F}_E = \hat{F}_E(\hat{t})$ and $\hat{F}_I = \hat{F}_I(\hat{t})$, while the volume, contact radius, and contact angle are denoted by $\hat{V} = \hat{V}(\hat{t})$, $\hat{R} = \hat{R}(\hat{t})$, and $\hat{\theta} = \hat{\theta}(\hat{t})$, respectively. The droplet is deposited onto the surface of the substrate at $\hat{t} = 0$, and thereafter undergoes mass loss due to simultaneous evaporation and imbibition. We do not consider the relatively short initial period during which the droplet rapidly adjusts to its quasi-static shape after it is deposited.

We non-dimensionalise and scale the variables appropriately for a thin droplet according to

$$\begin{aligned} r &= \frac{\hat{r}}{\hat{R}_0}, \quad z = \frac{\hat{z}}{\hat{\theta}_0 \hat{R}_0}, \quad V = \frac{\hat{V}}{\hat{\theta}_0 \hat{R}_0^3}, \quad R = \frac{\hat{R}}{\hat{R}_0}, \quad \theta = \frac{\hat{\theta}}{\hat{\theta}_0}, \quad t = \frac{\hat{U}_{\text{ref}} \hat{t}}{\hat{R}_0}, \quad u = \frac{\hat{u}}{\hat{U}_{\text{ref}}}, \\ w &= \frac{\hat{w}}{\hat{U}_{\text{ref}} \hat{\theta}_0}, \quad p = \frac{\hat{R}_0(\hat{p} - \hat{p}_\infty)}{\hat{\gamma} \hat{\theta}_0}, \quad J_E = \frac{\hat{J}_E}{\hat{J}_{E,\text{ref}}}, \quad J_I = \frac{\hat{J}_I}{\hat{J}_{I,\text{ref}}}, \quad F_E = \frac{\hat{F}_E}{\hat{R}_0^2 \hat{J}_{E,\text{ref}}}, \\ F_I &= \frac{\hat{F}_I}{\hat{R}_0^2 \hat{J}_{I,\text{ref}}}, \end{aligned} \tag{2.2}$$

where $\hat{U}_{\text{ref}}$ is an appropriate characteristic radial velocity scale, $\hat{p}_\infty$ is the constant atmospheric pressure, $\hat{J}_{E,\text{ref}}$ is an appropriate characteristic local evaporation mass flux scale for the evaporation of liquid from the free surface of the droplet into the atmosphere, and $\hat{J}_{I,\text{ref}}$ is an appropriate characteristic local imbibition mass flux scale for the imbibition of liquid from the base of the droplet into the substrate. The dimensionless ratios that characterise evaporation and imbibition, denoted by $\mathcal{E}$ and $\mathcal{I}$, hereafter

referred to as the evaporation number and the imbibition number, are defined by

$$\mathcal{E} = \frac{\hat{J}_{\text{E,ref}}}{\hat{\rho}\hat{\theta}_0\hat{U}_{\text{ref}}} \quad \text{and} \quad \mathcal{I} = \frac{\hat{J}_{\text{I,ref}}}{\hat{\rho}\hat{\theta}_0\hat{U}_{\text{ref}}}, \quad (2.3)$$

respectively, where $\hat{\rho}$ is the constant density of the liquid. For clarity, we note that the nondimensionalisation always scales on the dominant process so that either $\mathcal{E} = 1$ or $\mathcal{I} = 1$, and in the figures throughout this thesis we adopt the presentation choice of fixing $\mathcal{E} = 1$ while varying $\mathcal{I}$. We note that large values, such as $\mathcal{I} = 2^{15}$, fall outside the $O(1)$ regime and are included to illustrate the behaviour of the models investigated throughout this thesis under increasingly strong imbibition. Furthermore, because the plotted solutions are rescaled over the droplet lifetime, varying $\mathcal{I}$ in this way corresponds to examining the weak and strong evaporation and imbibition limits, respectively. Before defining $\hat{U}_{\text{ref}}$, $\hat{J}_{\text{E,ref}}$, $\hat{J}_{\text{I,ref}}$, and appropriate characteristic timescales for evaporation and imbibition, we first state the key assumptions and derive the hydrodynamic problem and the global mass balance equation for a droplet undergoing simultaneous evaporation and imbibition.

2.4 The Hydrodynamic Problem

In this section, we describe the evolution of, and the flow within, a thin sessile droplet undergoing simultaneous evaporation and imbibition. Specifically, we consider the situation in which the droplet is sufficiently small that the effect of gravity is negligible and surface tension is sufficiently strong that the free surface of the droplet evolves quasi-statically. More specifically, we consider situations in which the appropriately defined Bond number Bo and capillary number Ca , namely

$$\text{Bo} = \frac{\hat{\rho}\hat{g}\hat{R}_0^2}{\hat{\gamma}} \quad \text{and} \quad \text{Ca} = \frac{\hat{\mu}\hat{U}_{\text{ref}}}{\hat{\theta}_0^3\hat{\gamma}}, \quad (2.4)$$

respectively, are both small and satisfy $\hat{\theta}_0^2$, $\text{Bo} \ll \text{Ca} \ll 1$, where $\hat{g}$ is the magnitude of acceleration due to gravity and $\hat{\mu}$ is the constant dynamic viscosity of the liquid.

Throughout this thesis we assume that the droplet remains in the thin-film regime,

meaning that its aspect ratio is $O(\hat{\theta}_0)$ and that gravity and viscous stresses are weak compared with surface tension. In the asymptotic regime defined by $\hat{\theta}_0^2, \text{Bo} \ll \text{Ca} \ll 1$, the free surface evolves quasi-statically and the lubrication approximation is formally valid. For millimetre-scale water droplets these conditions are not strictly satisfied: with $\hat{R}_0 \sim 1 \text{ mm}$, $\hat{\rho} = 1000 \text{ kg m}^{-3}$, $\hat{\mu} = 10^{-3} \text{ Pa s}$, $\hat{\gamma} = 0.072 \text{ N m}^{-1}$, $\hat{\theta}_0 \approx 10^\circ$ ($\hat{\theta}_0 \approx 0.17$), and $\hat{U}_{\text{ref}} \sim 10^{-3} \text{ m s}^{-1}$, we obtain $\text{Bo} \approx 1.4 \times 10^{-3}$ and $\text{Ca} \approx 1.4 \times 10^{-5}$, while $\hat{\theta}_0^2 \approx 3 \times 10^{-2}$ is larger than both numbers. Thus the droplets are small enough that gravity is weak and the free surface evolves quasi-statically, but they do not satisfy $\hat{\theta}_0^2, \text{Bo} \ll \text{Ca} \ll 1$. Nevertheless, the lubrication-based model built on the three valid assumptions gives good quantitative agreement with experiments, indicating that violation of the formal ordering does not strongly affect the leading-order behaviour.

We seek an asymptotic solution for the pressure p in the form

$$p = p^{(0)}(r, z, t) + \text{Ca } p^{(1)}(r, z, t) + O\left(\hat{\theta}_0^2, \text{Bo}, \text{Ca}^2\right), \quad (2.5)$$

with corresponding expressions for the other variables. However, since the pressure p and the concentration of particles $\phi = \phi(r, z, t)$ introduced subsequently in Section 2.8 are the only quantities that we require beyond leading order, for clarity, we omit the superscript “(0)” on all of the other leading-order variables.

At leading order in Ca , the Stokes equations yield $\partial p^{(0)}/\partial r = \partial p^{(0)}/\partial z = 0$, and hence the leading-order pressure is independent of r and z . Therefore, $p^{(0)} = p^{(0)}(t)$ is given by the normal stress condition at the free surface to be

$$p^{(0)} = -\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right). \quad (2.6)$$

Hence, the free surface of the droplet $h(r, t)$ satisfies

$$\frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial h}{\partial r} \right) \right] = 0 \quad (2.7)$$

subject to $h = 0$ and $\partial h/\partial r = -\theta$ at $r = R$. An additional requirement is that $h(0, t)$ must be finite at $r = 0$, and hence the shape of the free surface takes the familiar

paraboloidal form

$$h = \frac{\theta(R^2 - r^2)}{2R}. \quad (2.8)$$

Evaluating the pressure (2.6) using (2.8) yields

$$p^{(0)} = \frac{2\theta}{R}. \quad (2.9)$$

We note that the leading-order pressure given by (2.9) is spatially uniform. The volume $V = V(t)$ of the droplet is given by

$$V = 2\pi \int_0^R h(r, t) r \, dr = \frac{\pi\theta R^3}{4}. \quad (2.10)$$

At leading order in the thin-film limit, the continuity and Stokes equations reduce to the familiar axisymmetric lubrication equations, namely

$$\frac{1}{r} \frac{\partial(ru)}{\partial r} + \frac{\partial w}{\partial z} = 0, \quad \frac{\partial^2 u}{\partial z^2} = \frac{\partial p^{(1)}}{\partial r}, \quad \frac{\partial p^{(1)}}{\partial z} = 0, \quad (2.11)$$

subject to the tangential stress condition,

$$\frac{\partial u}{\partial z} = 0 \quad \text{at} \quad z = h \quad \text{for} \quad 0 \leq r \leq R, \quad (2.12)$$

and the kinematic condition,

$$\frac{\partial h}{\partial t} + u \frac{\partial h}{\partial r} - w = -\mathcal{E} J_E \quad \text{at} \quad z = h \quad \text{for} \quad 0 \leq r \leq R, \quad (2.13)$$

on the free surface, together with a no-slip condition,

$$u = 0 \quad \text{on} \quad z = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.14)$$

and a penetration condition,

$$w = -\mathcal{I} J_I \quad \text{on} \quad z = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.15)$$

are imposed at the solid-liquid interface (i.e. on the surface of the substrate within the footprint of the droplet). The penetration condition (2.15) is a key feature of the present model and couples the flow within droplet to the flow within the substrate. Applying conditions (2.12), (2.14), and (2.15) to the solutions of (2.11), the radial and axial components of the flow within the droplet are given by

$$u = -\frac{(2h-z)z}{2} \frac{\partial p^{(1)}}{\partial r}, \quad w = \frac{z^2}{6r} \frac{\partial}{\partial r} \left((3h-z)r \frac{\partial p^{(1)}}{\partial r} \right) - \mathcal{I}J_{\text{I}}, \quad (2.16)$$

respectively. The kinematic condition (2.13) can be rewritten as

$$\frac{\partial h}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (rQ) = -(\mathcal{E}J_{\text{E}} + \mathcal{I}J_{\text{I}}), \quad (2.17)$$

where $Q = Q(r, t)$ is the local radial volume flux of liquid given by

$$Q = \int_0^h u \, dz = -\frac{h^3}{3} \frac{\partial p^{(1)}}{\partial r}. \quad (2.18)$$

The depth-averaged radial velocity $\bar{u} = \bar{u}(r, t)$, is given by

$$\bar{u} = \frac{1}{h} \int_0^h u \, dz = \frac{Q}{h}. \quad (2.19)$$

We note that it will be convenient to rearrange and integrate the kinematic condition (2.13) to express Q as

$$Q = -\frac{1}{r} \int_0^r \left(\mathcal{E}J_{\text{E}} + \mathcal{I}J_{\text{I}} + \frac{\partial h}{\partial t} \right) r \, dr. \quad (2.20)$$

Using (2.18) to eliminate the first-order pressure $p^{(1)}$ from the expression for u in (2.16) and then evaluating the integral in the expression for w in (2.16) yields

$$u = \frac{3Q(2h-z)z}{2h^3}, \quad w = -\frac{z^2}{2r} \frac{\partial}{\partial r} \left[\frac{rQ(3h-z)}{h^3} \right] - \mathcal{I}J_{\text{I}}. \quad (2.21)$$

Integrating the kinematic condition (2.17) from $r = 0$ to $r = R$ leads to the global

mass balance equation

$$\frac{dV}{dt} = -2\pi \int_0^R (\mathcal{E}J_E + \mathcal{I}J_I) r \, dr, \quad (2.22)$$

and substitution of the expression for the droplet volume (2.10) into (2.22) yields an evolution equation for R and θ , namely

$$\frac{d(\theta R^3)}{dt} = -8 \int_0^R (\mathcal{E}J_E + \mathcal{I}J_I) r \, dr. \quad (2.23)$$

However, (2.23) is only one equation for two unknowns, and so in order to determine the evolution, and hence the lifetime, of a droplet we must either determine or (as we do throughout thesis) specify the manner (i.e., the mode) in which the droplet evolves as it undergoes mass loss into the atmosphere and/or the substrate.

2.5 Modes of Evolution

Throughout this thesis, we classify droplet evolution into modes, each defined by simple constraints on the contact radius and contact angle. These classifications provide an analytically tractable framework for modelling and analysis. However, as discussed in this section, these modes are not purely theoretical and are observed in experiments on both evaporating and/or imbibing droplets. In many cases, a droplet will spend the majority of its evolution in one (or more) of these modes before transitioning to a final stage in which both the contact radius and contact angle decrease simultaneously (see, for example, Johnson *et al.* [21]). It should, of course, be noted that these modes are not the only way in which droplets can evolve. In particular when a droplet imbibes on porous substrates, several investigations, such as Wang *et al.* [223], Léang [3], and Tan [124] have observed droplet evolutions in which the contact radius and contact angle decrease simultaneously throughout the evolution, without a prolonged phase which can be easily classified into one of the modes considered in this thesis. Similarly, when a droplet evaporates and imbibes, Gonçalves *et al.* [224], and Heinz *et al.* [41, 42] observed droplet evolutions in which the contact radius and contact angle decrease

simultaneously throughout the evolution.

The modes of evolution which have received the most attention within the literature are the so-called extreme modes, namely the constant contact radius (CR) mode and the constant contact angle (CA) mode. In the CR mode the contact line remains pinned at the initial value $\hat{R} = \hat{R}_0$ and the contact angle decreases to zero. In contrast, in the CA mode the contact angle remains constant, and equal to its initial value $\hat{\theta} = \hat{\theta}_0$, and the contact radius decreases to zero.

There are also a variety of mixed modes in which both the contact radius and the contact angle vary. One combination of the extreme modes that frequently occurs in practice is the Stick–Slide (SS) mode, as described by Picknett & Bexon [48], and subsequently by Bourges *et al.* [50] (and many other authors, such as Nguyen *et al.* [225], Gelderblom *et al.* [226], Trybala *et al.* [227], Boulogne *et al.* [154, 155], Johnson *et al.* [21], and Bhattacharjee *et al.* [145]) in which the droplet first evolves in a CR phase with a pinned contact line $\hat{R} \equiv \hat{R}_0$ until the contact angle reaches a critical (receding) value, denoted by $\hat{\theta} = \hat{\theta}^*$, where $0 \leq \hat{\theta}^* \leq \hat{\theta}_0$. The time at which the contact line de-pins is denoted by $\hat{t} = \hat{t}^*$. Once the critical contact angle has been reached, the contact line de-pins, and thereafter the droplet evolves in a CA phase with a constant contact angle, $\hat{\theta} \equiv \hat{\theta}^*$, for the remainder of its evolution. The SS mode reduces to the CR mode when $\hat{\theta}^* = 0$, in which case the contact line never de-pins, and reduces to the CA mode when $\hat{\theta}^* = \hat{\theta}_0$, in which case the contact line immediately de-pins.

Another mode that occurs in practice is the Stick–Jump (SJ) mode, as described by Deegan *et al.* [53], (and many other authors, such as Moffat *et al.* [228], Shanahan & Sefiane [229], and Orejon *et al.* [230]), in which the droplet initially evolves in a CR phase with a pinned contact line. However, when the contact angle reaches a critical (minimum) value, denoted by $\hat{\theta} = \hat{\theta}_{\min}$, the contact line de-pins and jumps instantaneously inwards to a new position with a smaller contact radius, while the contact angle jumps instantaneously up to a critical (maximum) value, denoted by $\hat{\theta} = \hat{\theta}_{\max}$, where $0 \leq \hat{\theta}_{\min} \leq \hat{\theta}_{\max} = \hat{\theta}_0$. This pattern then repeats itself, with a (theoretically infinite) sequence of CR phases separated by a (theoretically infinite) sequence of instantaneous jump phases. The values of $\hat{R}$ and $\hat{\theta}$ in the n th CR phase

($n = 1, 2, 3, \dots$), which lasts from $\hat{t} = \hat{t}_{n-1}$ to $\hat{t} = \hat{t}_n$, where $\hat{t} = \hat{t}_n$, where $\hat{t}_0 = 0$ and $\hat{t} = \hat{t}_n$ ($n = 1, 2, 3, \dots$) is the time at which the n th jump phase occurs, are denoted by $\hat{R}_n$ and $\hat{\theta}_n = \hat{\theta}_n(\hat{t})$, respectively, with $\hat{R}_1 = \hat{R}_0$ and $\hat{\theta}_1 = \hat{\theta}_0 = \hat{\theta}_{\max}$, where $0 \leq \hat{\theta}_{\min} \leq \hat{\theta}_{\max}$. The SJ mode incorporates the CR and CA modes as special cases. Specifically, the SJ mode reduces to the CR mode when $\hat{\theta}_{\min} = 0$, and reduces to the CA mode in the limit $\hat{\theta}_{\min} \rightarrow \hat{\theta}_{\max}^- = \hat{\theta}_0^-$.

Figure 2.2 shows sketches of the evolutions of the free surface, contact radius, and contact angle in the four modes discussed. The lifetimes of a droplet evolving in the CR, CA, SS, and SJ modes are denoted by $\hat{t}_{\text{CR}}$, $\hat{t}_{\text{CA}}$, $\hat{t}_{\text{SS}}$, and $\hat{t}_{\text{SJ}}$, respectively.

While the occurrence of these modes is firmly established for a droplet evaporating on a solid substrate (see, for example, Wilson & D'Ambrosio [17]) the same cannot be said for a droplet evaporating and/or imbibing on a porous substrate. Hence, we summarise some of the key experimental investigations which observe these modes for a droplet undergoing imbibition or simultaneous evaporation and imbibition.

Over the past thirty years, the imbibition of droplets into various porous substrates has been experimentally investigated. A major contribution by Denesuk *et al.* [118] investigated the imbibition of silicone oil droplets on thick, initially dry, porous soda-lime-silicate substrates with the CR, CA, and SS modes observed. The forced imbibition of glycerol-water droplets on thick, initially dry, porous polycarbonate and polyvinylidene fluoride (PVDF) substrates was investigated by Bacri & Brochard-Wyatt [128] with the SS mode observed. The imbibition of silicon oil droplets on thin and thick, initially dry, porous cellulose nitrate substrates was investigated by Starov *et al.* [39,132] with the droplets found to evolve in the CA mode. Similarly, Starov *et al.* [114] investigated the imbibition of silicone oil droplets on thin, flooded, porous substrates and also observed the CA mode. The imbibition of water droplets on thick, initially dry, cellulose porous substrates was investigated by Clarke *et al.* [130], with the CR mode observed. Similarly, the imbibition of water droplets on thick, initially dry, porous powder bed substrates was investigated by Hapgood *et al.* [133], with the CR mode observed. Kumar & Desphande [123] investigated the imbibition of silicone oil droplets on thin, initially dry, porous glass-fibre mat substrates and observed the CR, CA, and

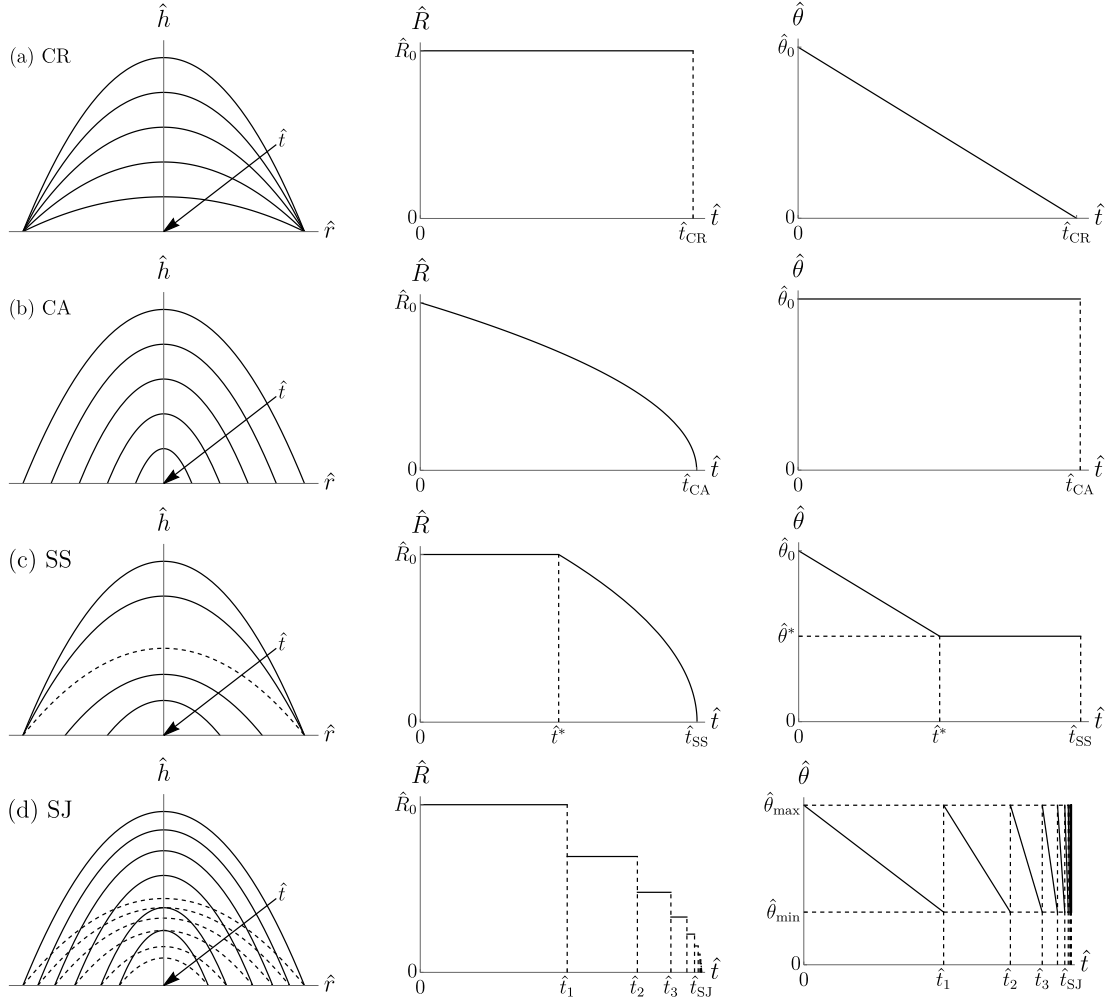


Figure 2.2: Sketches of the evolutions of the free surface $\hat{h}(\hat{r}, \hat{t})$, the contact radius $\hat{R}(\hat{t})$, and the contact angle $\hat{\theta}(\hat{t})$, respectively. Each row of the figure corresponds to a different mode of evolution; (a) the CR mode, (b) the CA mode, (c) the SS mode, and (d) the SJ mode. The dashed lines in (a) and (b) correspond to the lifetime of the droplet. The dashed lines in (c) correspond to the instant $\hat{t} = \hat{t}^*$ at which the droplet contact line de-pins in the SS mode and to the lifetime of the droplet. The dashed lines in (d) correspond to the instants $\hat{t} = \hat{t}_n (n = 1, 2, 3, \dots)$ at which the droplet contact line de-pins and jumps inwards from $\hat{R}_n$ to $\hat{R}_{n+1} (< \hat{R}_n)$ and to the lifetime of the droplet.

SS modes. The imbibition of blood droplets on thin, initially dry, porous filter paper substrates was investigated by Chao *et al.* [231], with the CA mode observed. The imbibition and deposition patterns of colloidal droplets on thick hydrogels was examined by Boulogne *et al.* [154,155], with the SS mode observed. The imbibition of water droplets on thick, initially dry, porous limestone substrates was investigated by Lee *et al.* [4], with the CR mode observed. The imbibition of particle-laden water droplets on thin, initially dry, porous filter paper substrates was investigated by Kumar *et al.* [232], with the CA mode observed. To the best of our knowledge, no evolution in the SJ mode has been reported for a droplet imbibing into a porous substrate in the literature, even though it is commonly observed for a droplet evaporating on equally spaced pillars (see Orejon *et al.* [230]), which closely resemble vertically aligned, cylindrical pores.

In contrast to the pure evaporation and imbibition problems, relatively few experimental studies have investigated the simultaneous effect of evaporation and imbibition on droplet evolution. The evaporation and imbibition of ink droplets on thick, initially dry, porous powder bed substrates was investigated by Dou *et al.* [186] and Dou & Derby [187]. Similarly, Pack *et al.* [1] investigated the evaporation and imbibition of water droplets on initially dry, porous anodic aluminium oxide substrates. Willis *et al.* [10] investigated the evaporation and imbibition of (2-chloroethyl) sulfide (commonly referred to as distilled mustard gas or “HD”, in military terminology) droplets on thick, initially dry, porous silicone substrates. Similarly, Richards *et al.* [11] investigated the evaporation and imbibition of trichloroethylene and tetrachloroethylene droplets on thick, initially dry, porous butyl-rubber substrates. Li *et al.* [6] investigated the evaporation and imbibition of particle-laden water droplets on thick, initially dry, nano-porous silica substrates. In all of the investigations discussed in this paragraph the CR mode was observed.

2.6 The Evaporative Problem

In this section, we describe the evaporation of liquid from the free surface of a thin droplet into the atmosphere according to the basic version of the well-known diffusion-limited model, as sketched in Figure 2.3, with constant diffusion coefficient $\hat{D}$. The

concentration of vapour in the atmosphere is denoted by $\hat{c} = \hat{c}(\hat{r}, \hat{z}, \hat{t})$. The constant concentration of vapour at the free surface of the droplet $\hat{z} = \hat{h}(\hat{r}, \hat{t})$ is denoted by $\hat{c} = \hat{c}_{\text{sat}}$, and the constant far-field concentration is denoted by $\hat{c} = \hat{c}_{\infty}$. The physical quantities $\hat{D}$, $\hat{c}_{\text{sat}}$, and $\hat{c}_{\infty}$ are all assumed to be isotropic and constant in the basic version of the diffusion-limited model considered in the present work. Before proceeding further, we introduce the additional non-dimensional variables involved in the evaporative problem, namely

$$c = \frac{\hat{c} - \hat{c}_{\infty}}{\hat{c}_{\text{sat}} - \hat{c}_{\infty}} \quad \text{and} \quad z^{\text{a}} = \frac{\hat{z}}{\hat{R}_0}, \quad (2.24)$$

where z^{a} denotes the non-dimensional z coordinate in the atmosphere. Appropriate choices of $\hat{U}_{\text{E,ref}}$ and $\hat{J}_{\text{E,ref}}$ for the diffusion-limited evaporation problem are given by

$$\hat{U}_{\text{E,ref}} = \frac{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})}{\hat{\rho}\hat{\theta}_0\hat{R}_0} \quad \text{and} \quad \hat{J}_{\text{E,ref}} = \hat{\rho}\hat{\theta}_0\hat{U}_{\text{E,ref}} = \frac{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})}{\hat{R}_0}. \quad (2.25)$$

(see, for example, Wilson & D'Ambrosio [17]). An appropriate characteristic timescale for the diffusion-limited evaporation of a thin droplet is

$$\hat{t}_{\text{E,ref}} = \frac{\hat{\rho}\hat{\theta}_0\hat{R}_0^2}{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})} \quad (2.26)$$

(see, for example, Wilson & D'Ambrosio [17]). These scales are appropriate because they reflect the characteristic strength of the diffusive transport that drives evaporation and the corresponding internal flow required to replenish liquid at the free surface of a thin droplet.

Since the droplet is thin, the concentration of vapour $c = c(r, z^{\text{a}}, t)$ satisfies Laplace's equation in the upper half-space,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^{\text{a}2}} = 0 \quad \text{for} \quad z^{\text{a}} > 0, \quad (2.27)$$

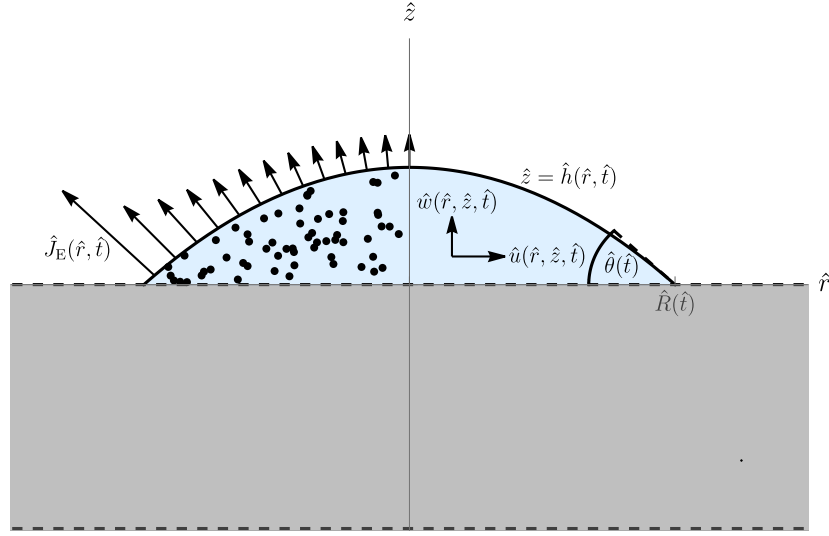


Figure 2.3: Sketch of a thin sessile particle-laden droplet evaporating on a solid substrate.

subject to the appropriate boundary and far-field conditions, namely,

$$c = 1 \quad \text{on} \quad z^a = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.28)$$

$$\frac{\partial c}{\partial z^a} = 0 \quad \text{on} \quad z^a = 0 \quad \text{for} \quad r > R, \quad (2.29)$$

$$c \rightarrow 0 \quad \text{as} \quad (r^2 + z^{a2})^{1/2} \rightarrow \infty. \quad (2.30)$$

Note that, in general, the boundary condition (2.28) applies on the free surface $z = h(r, t)$, but for a thin droplet, such as that considered throughout this thesis, it can be transferred to the plane $z^a = 0$ by Taylor expanding about $z^a = 0$. Equations (2.27)–(2.30) may be solved to obtain the well-known solution for the concentration of vapour in the atmosphere (see, for example, Carslaw & Jager [233]), namely

$$c = \frac{2}{\pi} \arcsin \frac{2}{[(R+r)^2 + z^{a2}]^{1/2} + [(R-r)^2 + z^{a2}]^{1/2}}. \quad (2.31)$$

The local evaporation mass flux is then given by

$$J_E = -\frac{\partial c}{\partial z^a} = \frac{2}{\pi} (R^2 - r^2)^{-1/2} \quad \text{on} \quad z^a = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.32)$$

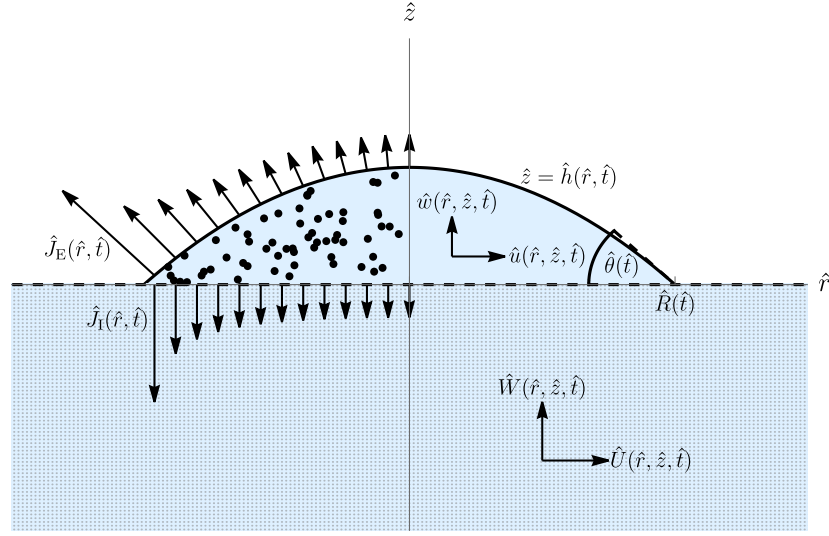


Figure 2.4: Sketch of a thin sessile particle-laden droplet evaporating and imbibing on an infinitely thick, isotropic, flooded, porous substrate.

and hence the global evaporation mass flux is

$$F_E = 2\pi \int_0^R J_E r \, dr = 4R. \quad (2.33)$$

2.7 The Imbibition Problem

In this section, we describe the imbibition of liquid from the base of a thin sessile droplet into the three porous substrates introduced in Section 1.3: (i) an infinitely thick, isotropic, flooded, porous substrate; (ii) a finitely thick, anisotropic, initially dry, porous substrate; and (iii) a finitely thick, anisotropic, flooded, porous substrate. Figures 2.4, 2.5, and 2.6 show sketches of a thin sessile particle-laden droplet evaporating and imbibing on these three substrates, respectively.

2.7.1 An infinitely thick, isotropic, flooded, porous substrate

In this subsection, we describe the imbibition of liquid from the base of a thin sessile droplet into an infinitely thick, isotropic, flooded, porous substrate with interconnected pores.

The radial and axial components of the macroscopic velocity within the substrate are

denoted by $\hat{U} = \hat{U}(\hat{r}, \hat{z}, \hat{t})$ and $\hat{W} = \hat{W}(\hat{r}, \hat{z}, \hat{t})$, respectively, and the pressure within the substrate is denoted by $\hat{P} = \hat{P}(\hat{r}, \hat{z}, \hat{t})$. The constant porosity of the substrate, denoted by φ , $0 < \varphi < 1$, is a measure of the volume-averaged fraction of the interconnected pores within the substrate, and the constant permeability of the substrate, denoted by $\hat{k}$, is an intrinsic property of the substrate that describes the viscous resistance to the flow through the pores. In general, a larger internal pore surface area per unit volume leads to a larger friction within the substrate and, hence, a lower permeability. The pressure at the surface of the substrate within the footprint of the droplet is equal to the (spatially uniform) pressure at the base of the droplet, and the constant far-field pressure (assumed to be equal to the atmospheric pressure) is denoted by $\hat{P}_\infty (= \hat{p}_\infty)$. The physical quantities φ , $\hat{k}$, and $\hat{P}_\infty$ are all assumed to be isotropic and constant in the imbibition model described in this section. Before proceeding further, we introduce the additional non-dimensional variables involved in the imbibition problem, namely

$$U = \frac{\hat{\rho}\hat{U}}{\hat{J}_{\text{I,ref}}}, \quad W = \frac{\hat{\rho}\hat{W}}{\hat{J}_{\text{I,ref}}}, \quad P = \frac{\hat{R}_0(\hat{P} - \hat{P}_\infty)}{\hat{\gamma}\hat{\theta}_0}, \quad \text{and} \quad z^s = \frac{\hat{z}}{\hat{R}_0}, \quad (2.34)$$

where $z^s (= z^a)$ denotes the non-dimensional z coordinate in the substrate. Appropriate choices of $\hat{U}_{\text{I,ref}}$ and $\hat{J}_{\text{I,ref}}$ for the imbibition problem are given by

$$\hat{U}_{\text{I,ref}} = \frac{\hat{\gamma}\hat{k}}{\hat{\mu}\hat{R}_0^2} \quad \text{and} \quad \hat{J}_{\text{I,ref}} = \hat{\rho}\hat{\theta}_0\hat{U}_{\text{I,ref}} = \frac{\hat{\rho}\hat{\gamma}\hat{k}\hat{\theta}_0}{\hat{\mu}\hat{R}_0^2}. \quad (2.35)$$

An appropriate characteristic timescale for the imbibition of a thin sessile droplet on an infinitely thick, isotropic, flooded, porous substrate is

$$\hat{t}_{\text{I,ref}} = \frac{\hat{\mu}\hat{R}_0^3}{\hat{k}\hat{\gamma}}. \quad (2.36)$$

Throughout this thesis, Darcy's law is used to describe the flow of liquid within the substrate, and so the radial and axial components of the macroscopic velocity are

related to the pressure according to

$$U = -\frac{1}{\varphi} \frac{\partial P}{\partial r} \quad \text{and} \quad W = -\frac{1}{\varphi} \frac{\partial P}{\partial z^s}. \quad (2.37)$$

Local conservation of mass of liquid within the substrate leads to the appropriate continuity equation,

$$\frac{1}{r} \frac{\partial (rU)}{\partial r} + \frac{\partial W}{\partial z^s} = 0, \quad (2.38)$$

and substitution of (2.37) into (2.38) shows that the pressure within the porous substrate $P = P(r, z^s, t)$ satisfies Laplace's equation in the lower half-space,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial P}{\partial r} \right) + \frac{\partial^2 P}{\partial z^{s2}} = 0 \quad \text{for} \quad z^s < 0, \quad (2.39)$$

subject to the appropriate boundary and far-field conditions, namely

$$P = p^{(0)} \quad \text{on} \quad z^s = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.40)$$

$$\frac{\partial P}{\partial z^s} = 0 \quad \text{on} \quad z^s = 0 \quad \text{for} \quad r \geq R, \quad (2.41)$$

$$P \rightarrow 0 \quad \text{as} \quad (r^2 + z^{s2})^{1/2} \rightarrow \infty. \quad (2.42)$$

Analogous to solving equations (2.28)–(2.30) to obtain the solution for the concentration of vapour in the atmosphere given by (2.31), equations (2.40)–(2.42) may be solved to obtain the corresponding solution for the pressure within the substrate, namely

$$P = \frac{4\theta}{\pi R} \arcsin \frac{2R}{[(R+r)^2 + z^{s2}]^{1/2} + [(R-r)^2 + z^{s2}]^{1/2}}. \quad (2.43)$$

The local imbibition mass flux is then given by

$$J_I = \frac{\partial P}{\partial z^s} = \frac{4\theta}{\pi R} (R^2 - r^2)^{-1/2} \quad \text{on} \quad z^s = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.44)$$

and hence the global imbibition mass flux is

$$F_I = 2\pi \int_0^R J_I r \, dr = 8\theta. \quad (2.45)$$

Note that, in contrast to the global evaporation mass flux F_E given by (2.33), which depends on R but not θ , the global imbibition mass flux F_I given by (2.45) depends on θ but not R . However, both depend on t parametrically via either R or θ .

The boundary condition (2.40) on the substrate–atmosphere interface is a modelling idealisation introduced to avoid resolving the detailed behaviour of partially saturated regions of the substrate. In the present formulation, liquid that enters the porous substrate beneath the droplet is assumed not to return to the surface or be displaced out of the pores, so the exposed region of the substrate is treated as effectively sealed. A more natural condition would be $P = 0$ (atmospheric pressure), but imposing this would require a full description of pore-scale saturation, redistribution, and possible back-flow, which lies outside the scope of the current model. Further discussion of related idealisations can be found in Davis & Hocking [35], and a more complete treatment of the substrate–air interface would be a natural extension for future work.

2.7.2 A finitely thick, anisotropic, initially dry, porous substrate

In this subsection, we describe the imbibition of liquid from the base of a thin sessile droplet into a finitely thick, anisotropic, initially dry, porous substrate, as discussed in Section 1.4. In this situation the pores are vertically aligned and non-connected, and as a result flow only occurs within the substrate in the vertical direction. The axial component of the macroscopic velocity within the substrate is denoted by $\hat{W} = \hat{W}(\hat{t})$ and the pressure within the substrate is denoted by $\hat{P} = \hat{P}(\hat{z}, \hat{t})$. The pressure at the surface of the substrate within the footprint of the droplet is equal to the pressure at the base of the droplet given by equation (2.6), and hence is spatially uniform, with the pressure at the wetting front, denoted by $\hat{z} = -\hat{H}(\hat{t})$ being equal to $\hat{P} = -\hat{P}_c$, where $\hat{P}_c$ is the constant capillary pressure within each pore. The capillary pressure is defined as the tendency of a porous substrate to suck in liquid (i.e., the wetting phase) or to

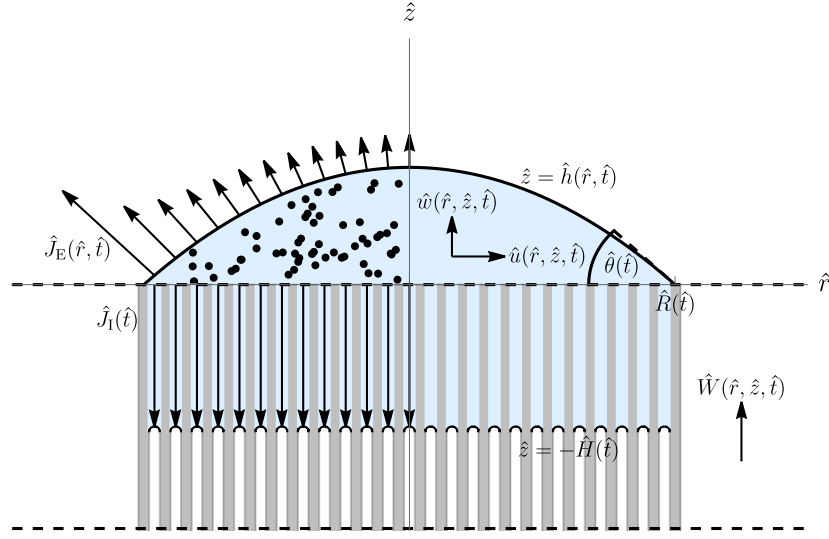


Figure 2.5: Sketch of a thin sessile particle-laden droplet evaporating and imbibing on a finitely thick, anisotropic, initially dry, porous substrate.

repel air (i.e., the non-wetting phase) (see, for example, Bear [34]). We assume the substrate thickness, denoted by $\hat{d}$, exceeds maximum depth of the wetting fronts once the droplet volume is fully depleted.

Throughout this thesis, we keep our analysis as general as possible and do not explicitly specify the exact geometry of the pores and instead, in the spirit of Darcy's original description, consider $\hat{k}$ and $\hat{P}_c$ to be experimentally determined variables. However, we highlight the situation often used within the literature to mathematically describe the permeability and capillary pressure, in which the pores within the substrate are described as vertically aligned, cylindrical, non-connected, and of constant cross-sectional area, given by

$$\hat{k} = \frac{\varphi \hat{a}^2}{8} \quad \text{and} \quad \hat{P}_c = \frac{2\hat{\gamma} \cos \hat{\alpha}}{\hat{a}}, \quad (2.46)$$

respectively, where $\hat{a}$ is the constant radius of the cross-sectional area of each pore and $\hat{\alpha}$ is the constant contact angle at the gas-liquid interface within each pore (see, for example, Alleborn & Raszillier [135]). Alternatively, in situations in which the solid matrix within the porous substrate is described as a packed bed of spheres of uniform radius, and the net-average flow occurs in the axial direction, the permeability

is often estimated from the Carman–Kozeny equation (see, for example, Kozeny [234], Carman [235], Bear [34], Xiao *et al.* [142], and Gambaryan-Roisman [20]).

We follow the conventional approach (see, for example, Denesuk *et al.* [118], Alleborn & Rasziller [135], and Zadrazil *et al.* [139]) and assume that the pore radius is orders of magnitude smaller than the radius of the droplet. Hence, $(\hat{p}^{(0)} - \hat{p}_\infty)/\hat{P}_c \ll 1$ and the pressure within the droplet and atmospheric pressure are neglected in subsequent analysis. Before proceeding further, we introduce the additional non-dimensional variables involved in the imbibition problem, namely

$$P = \frac{\hat{P}}{\hat{P}_c}, \quad W = \frac{\hat{\rho}\hat{W}}{\hat{J}_{\text{I,ref}}}, \quad \text{and} \quad z^s = \frac{\hat{z}\varphi}{\hat{\theta}_0\hat{R}_0}, \quad (2.47)$$

where we denote the non-dimensional z coordinate z^s in the porous substrate with a superscript “s”.

Appropriate choices of $\hat{U}_{\text{I,ref}}$ and $\hat{J}_{\text{I,ref}}$ for the imbibition problem are given by

$$\hat{U}_{\text{I,ref}} = \frac{\varphi\hat{k}\hat{P}_c}{\hat{\mu}\hat{\theta}_0^2\hat{R}_0} \quad \text{and} \quad \hat{J}_{\text{I,ref}} = \hat{\rho}\hat{\theta}_0\hat{U}_{\text{I,ref}} = \frac{\hat{\rho}\varphi\hat{k}\hat{P}_c}{\hat{\mu}\hat{\theta}_0\hat{R}_0}. \quad (2.48)$$

A characteristic timescale for the imbibition of a thin sessile droplet on a finitely thick, anisotropic, initially dry, porous substrate is

$$\hat{t}_{\text{I,ref}} = \frac{\hat{\mu}\hat{\theta}_0^2\hat{R}_0^2}{\varphi\hat{k}\hat{P}_c} \quad (2.49)$$

(see, for example, Denesuk *et al.* [118] and Middleman [127]). Mass conservation within the porous substrate is imposed by the continuity equation,

$$\frac{\partial W}{\partial z^s} = 0, \quad (2.50)$$

and the pressure within the porous substrate $P = P(r, z^s, t)$ satisfies a second-order linear homogeneous differential equation, namely

$$\frac{\partial^2 P}{\partial z^{s2}} = 0 \quad \text{for} \quad -H \leq z^s \leq 0, \quad (2.51)$$

subject to the appropriate boundary conditions, namely

$$P = 0 \quad \text{on} \quad z^s = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.52)$$

$$P = -1 \quad \text{on} \quad z^s = -H \quad \text{for} \quad 0 \leq r \leq R. \quad (2.53)$$

Equations (2.51) to (2.53) may be solved to obtain the corresponding solution for the pressure within the substrate, namely

$$P = \frac{z^s}{H}, \quad (2.54)$$

where the evolution of the wetting front is given by

$$\frac{\partial H}{\partial t} = -\varphi W = \frac{\partial P}{\partial z^s} = \frac{1}{H}, \quad (2.55)$$

and hence

$$H = (2t)^{1/2}. \quad (2.56)$$

We note that this is a well-known result for the evolution of the wetting front within a porous substrate (see, for example, Denesuk *et al.* [118] and Davis & Hocking [36]). The local imbibition mass flux is then given by

$$J_I = \frac{\partial P}{\partial z^s} = \left(\frac{1}{2t}\right)^{1/2} \quad \text{on} \quad z^s = 0 \quad \text{for} \quad 0 \leq r \leq R, \quad (2.57)$$

and hence the global imbibition mass flux is

$$F_I = 2\pi \int_0^R J_I r \, dr = \pi R^2 \left(\frac{1}{2t}\right)^{1/2}. \quad (2.58)$$

Note that, in contrast to the global imbibition flux given by (2.45), which depends on θ but not R , the global imbibition mass flux F_I given by (2.58) depends on R but not θ . However, (2.58) may depend on R or θ parametrically via t .

2.7.3 A finitely thick, anisotropic, flooded, porous substrate

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namely

$$W = \frac{\hat{\rho}\hat{W}}{\hat{J}_{\text{I,ref}}}, \quad P = \frac{\hat{R}_0(\hat{P} - \hat{P}_\infty)}{\hat{\gamma}\hat{\theta}_0}, \quad \text{and} \quad z^s = \frac{\hat{z}}{\hat{d}}, \quad (2.59)$$

where z^s denotes the non-dimensional z coordinate in the substrate. Appropriate choices of $\hat{U}_{\text{I,ref}}$ and $\hat{J}_{\text{I,ref}}$ for the imbibition problem are given by

$$\hat{U}_{\text{I,ref}} = \frac{\hat{\gamma}\hat{k}}{\hat{\mu}\hat{d}\hat{R}_0} \quad \text{and} \quad \hat{J}_{\text{I,ref}} = \hat{\rho}\hat{\theta}_0\hat{U}_{\text{I,ref}} = \frac{\hat{\rho}\hat{\gamma}\hat{k}\hat{\theta}_0}{\hat{\mu}\hat{d}\hat{R}_0}. \quad (2.60)$$

An appropriate characteristic timescale for the imbibition of a thin droplet on a finitely thick, anisotropic, flooded, porous substrate is

$$\hat{t}_{\text{I,ref}} = \frac{\hat{\mu}\hat{d}\hat{R}_0^2}{\hat{\gamma}\hat{k}} \quad (2.61)$$

(see, for example, Davis & Hocking [35]). Similarly to Sections 2.7.2 and 2.7.3, we use Darcy's law to describe the flow of liquid within the substrate, and so the axial component of the macroscopic velocity is given by equation (2.37). Hence, local conservation of mass of liquid within the substrate leads to the appropriate reduced continuity equation (2.50) and the pressure within the porous substrate satisfies the reduced one-dimensional Laplace equation given by (2.51) subject to the appropriate boundary conditions, namely

$$P = p^{(0)} \quad \text{for} \quad 0 \leq r \leq R \quad \text{on} \quad z^s = 0, \quad (2.62)$$

$$P = 0 \quad \text{for} \quad 0 \leq r \leq R \quad \text{on} \quad z^s = -1, \quad (2.63)$$

Equations (2.51), (2.62), and (2.63) may be solved to obtain the corresponding solution for the pressure within the substrate, namely

$$P = \frac{2\theta}{R}(z + 1). \quad (2.64)$$

The local imbibition mass flux is then given by

$$J_I = \frac{\partial P}{\partial z^s} = \frac{2\theta}{R} \quad \text{on } z^s = 0 \quad \text{for } 0 \leq r \leq R, \quad (2.65)$$

and hence the global imbibition mass flux is

$$F_I = 2\pi \int_0^R J_I r \, dr = 2\pi\theta R. \quad (2.66)$$

2.8 The Particle Transport and Deposition Problem

In this section, we describe the transport and deposition onto the substrate of a dilute suspension of neutrally-buoyant and hydrodynamically passive particles from a particle-laden droplet (see, for example, Kang *et al.* [78], Moore *et al.* [73], Wray *et al.* [72], and Wilson & D'Ambrosio [17]).

The concentration of particles per unit volume within the bulk of the droplet $\hat{\phi} = \hat{\phi}(\hat{r}, \hat{z}, \hat{t})$ satisfies an advection-diffusion equation subject to a penetration condition on the surface of the substrate and a no-flux condition on the free surface of the droplet. The concentration of particles per unit volume within the bulk of the droplet is non-dimensionalised according to $\phi = \hat{\phi}/\hat{\phi}_{\text{ref}}$, where $\hat{\phi}_{\text{ref}}$ is the spatial average of the initial concentration of particles. Hence $\phi = \phi(r, z, t)$ satisfies

$$\text{Pe}^* \left(\frac{\partial \phi}{\partial t} + u \frac{\partial \phi}{\partial r} + w \frac{\partial \phi}{\partial z} \right) = \frac{\hat{\theta}_0^2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \phi}{\partial r} \right) + \frac{\partial^2 \phi}{\partial z^2}, \quad (2.67)$$

where Pe^* is the appropriately defined reduced Péclet number that is the ratio of the characteristic advective and diffusive particle transport timescales, namely

$$\text{Pe}^* = \hat{\theta}_0^2 \text{Pe} = \frac{\hat{\theta}_0^2 \hat{R}_0 \hat{U}_{\text{ref}}}{\hat{D}_p}, \quad (2.68)$$

where $\hat{D}_p$ is the constant diffusivity of the particles within the droplet. For simplicity, in the present work we assume that particles do not pass into the substrate and that the accumulation of particles on the surface of the substrate does not inhibit the flow of liquid into the substrate, but both of these assumptions could be revisited in future

work. Hence (2.67) is subject to the boundary conditions

$$\frac{\partial \phi}{\partial z} = -\text{Pe}^* \mathcal{I} J_I \phi \quad \text{on} \quad z = 0 \quad (2.69)$$

and

$$\frac{1}{\left(1 + \hat{\theta}_0^2 (\partial h / \partial r)^2\right)^{1/2}} \left(\frac{\partial \phi}{\partial z} - \hat{\theta}_0^2 \frac{\partial h}{\partial r} \frac{\partial \phi}{\partial r} \right) = \text{Pe}^* \mathcal{E} J_E \phi \quad \text{on} \quad z = h. \quad (2.70)$$

We consider the regime in which diffusion of particles is faster than axial advection but slower than radial advection of particles. In other words, we consider the regime in which the reduced Péclet number satisfies $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$ (see, for example, Jensen & Grotberg [236] and D'Ambrosio *et al.* [82]). (In Chapter 6 we will consider the paths of the particles within the droplet in the alternative regime $\text{Pe}^* \gg 1$ in which diffusion of particles is slower than both radial and axial advection of particles, and hence at leading order diffusion of particles plays no role and the transport of particles is purely advective.) Hence, we seek an asymptotic solution for the concentration of particles ϕ in the form

$$\phi = \phi^{(0)}(r, z, t) + \text{Pe}^* \phi^{(1)}(r, z, t) + \mathcal{O}\left(\hat{\theta}_0^2, \text{Pe}^{*2}\right). \quad (2.71)$$

At leading order in Pe^* , equations (2.67), (2.69), and (2.70) reduce to

$$\frac{\partial^2 \phi^{(0)}}{\partial z^2} = 0 \quad (2.72)$$

subject to

$$\frac{\partial \phi^{(0)}}{\partial z} = 0 \quad \text{on} \quad z = 0 \quad \text{and} \quad z = h, \quad (2.73)$$

and hence the leading-order concentration $\phi^{(0)}$ is independent of z , i.e., $\phi^{(0)} = \phi^{(0)}(r, t)$.

At first order in Pe^* , equations (2.67), (2.69), and (2.70) reduce to

$$\frac{\partial^2 \phi^{(1)}}{\partial z^2} = \frac{\partial \phi^{(0)}}{\partial t} + u \frac{\partial \phi^{(0)}}{\partial r} \quad (2.74)$$

subject to

$$\frac{\partial \phi^{(1)}}{\partial z} = -\phi \mathcal{I} J_{\text{I}} \quad \text{on} \quad z = 0 \quad (2.75)$$

and

$$\frac{\partial \phi^{(1)}}{\partial z} = \phi \mathcal{E} J_{\text{E}} \quad \text{on} \quad z = h. \quad (2.76)$$

Integrating (2.74) with respect to z subject to (2.75) and (2.76), and omitting the superscript “(0)” for clarity, we arrive at the equation governing the evolution of the leading-order concentration of particles within the droplet, namely

$$\frac{\partial \phi}{\partial t} + \bar{u} \frac{\partial \phi}{\partial r} = \frac{\mathcal{E} J_{\text{E}} + \mathcal{I} J_{\text{I}}}{h} \phi. \quad (2.77)$$

Equation (2.77) can be written in characteristic form as

$$\frac{d\phi}{dt} = \frac{\mathcal{E} J_{\text{E}} + \mathcal{I} J_{\text{I}}}{h} \phi \quad \text{on the characteristics determined by} \quad \frac{dr}{dt} = \bar{u}, \quad (2.78)$$

subject to the initial condition $r = r_0$ ($0 \leq r_0 \leq 1$) and $\phi = \phi(r, 0) = \phi_0(r)$ at $t = 0$, where $r_0 = r_0(r, t)$ denotes the initial radial position of the particle that is at the radial position r at time t (see, for example, Boulogne *et al.* [79] and D’Ambrosio *et al.* [82]).

The mass of particles per unit area within the bulk of the droplet is given by ϕh , and hence the mass of particles in the bulk of the droplet, denoted by $M_{\text{drop}} = M_{\text{drop}}(t)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0^3 \hat{\phi}_{\text{ref}}$, is given by

$$M_{\text{drop}} = 2\pi \int_0^{R(t)} \phi(r, t) h(r, t) r \, dr, \quad (2.79)$$

which can alternatively be expressed as

$$M_{\text{drop}} = 2\pi \int_0^{r_0(R(t), t)} \phi(r, 0) h(r, 0) r \, dr. \quad (2.80)$$

The initial mass of particles in the bulk of the droplet is denoted by $M_0 = M_{\text{drop}}(0)$. For simplicity, in the remainder of the present work we take the initial concentration of particles in the bulk of the droplet to be spatially uniform, i.e., $\phi_0(r) \equiv 1$, in which

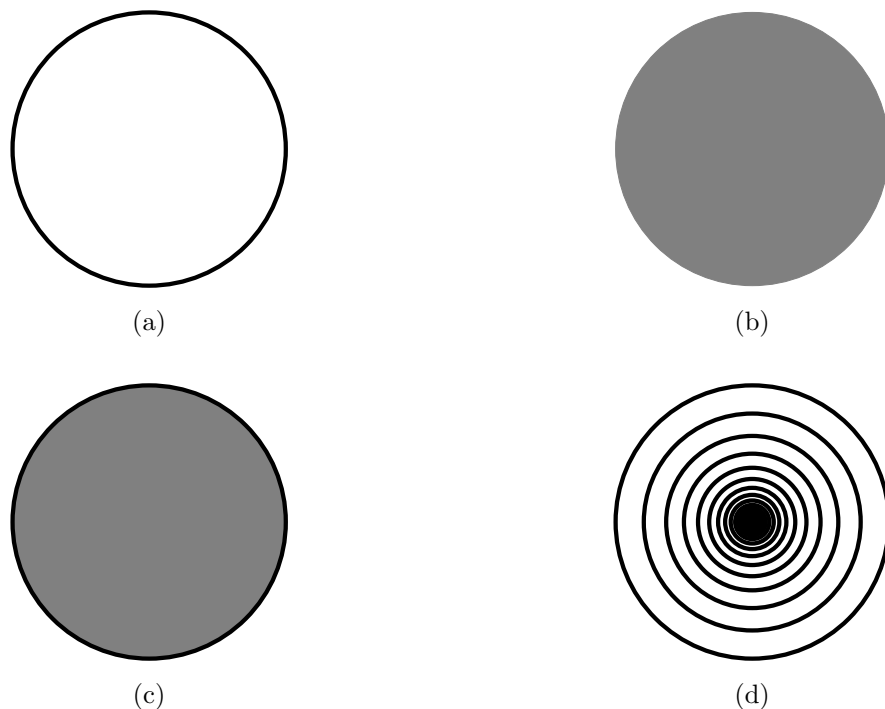


Figure 2.7: Sketches of the final deposit patterns arising from particle-laden droplets evolving in the CR, CA, SS, and SJ modes, respectively, namely (a) a ring deposit, (b) a distributed deposit, (c) a combined ring and distributed deposit, and (d) multiple ring deposits.

case M_0 is given by

$$M_0 = 2\pi \int_0^1 \phi_0(r)h(r,0)r \, dr = 2\pi \int_0^1 h(r,0)r \, dr = \frac{\pi}{4}. \quad (2.81)$$

The final deposit pattern (i.e., the pattern of particles left behind on the substrate after the droplet has completely evaporated and/or imbibed) depends on the manner (i.e., the mode) in which the droplet evolved. The four modes of evolution considered in the present work give rise to the four qualitatively different final deposit patterns sketched in Figure 2.7, namely a ring deposit, a distributed deposit, a combined ring and distributed deposit, and multiple ring deposits. In the next four subsections we describe how these four final deposit patterns arise from droplets evolving in the CR, CA, SS, and SJ modes, respectively.

2.8.1 Particle Deposition in the CR Mode

In the CR mode, the particles are deposited onto the substrate via the pinned contact line, resulting in the formation of a ring deposit at $r = 1$ (i.e., the well-known coffee-ring effect), as sketched in Figure 2.7(a). The mass flux of particles from the bulk of the droplet into the contact line is given by

$$\lim_{r \rightarrow 1^-} 2\pi\phi h \bar{u} r \quad (2.82)$$

(see, for example, Deegan *et al.* [54] and D'Ambrosio *et al.* [82]), and so the mass of particles in the ring deposit at time t , denoted by $M_{\text{ring}} = M_{\text{ring}}(t)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0^3 \hat{\phi}_{\text{ref}}$, is given by

$$M_{\text{ring}} = 2\pi \int_0^t \lim_{r \rightarrow 1^-} \phi(r, t) h(r, t) \bar{u}(r, t) r \, dt, \quad (2.83)$$

which can alternatively be expressed as

$$M_{\text{ring}} = 2\pi \int_{r_0(1, t)}^1 \phi(r, 0) h(r, 0) r \, dr. \quad (2.84)$$

Note that, since all of the particles are initially within the bulk of the droplet, but are all eventually transferred to the ring deposit, $M_{\text{ring}}(0) = 0$ and $M_{\text{ring}}(t_{\text{CR}}) = M_0$.

2.8.2 Particle Deposition in the CA Mode

In the CA mode, the particles are again deposited onto the substrate via the contact line, but, since the contact line is continuously receding, this results in the formation of a distributed deposit within the initial footprint of the droplet (i.e., in $0 \leq r < 1$), as sketched in Figure 2.7(b). The mass flux of particles from the bulk of the droplet into the contact line is given by

$$\lim_{r \rightarrow R(t)^-} 2\pi\phi h \left(\bar{u} - \frac{dR}{dt} \right) r \quad (2.85)$$

(see D'Ambrosio *et al.* [84]), and so the mass of particles in the distributed deposit that occupies the annular region $R(t) \leq r < 1$ at time t , denoted by $M_{\text{dist}} = M_{\text{dist}}(t)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0^3 \hat{\phi}_{\text{ref}}$, is given by

$$M_{\text{dist}} = 2\pi \int_0^t \lim_{r \rightarrow R(t)^-} \phi(r, t) h(r, t) \left(\bar{u}(r, t) - \frac{dR}{dt} \right) r \, dt, \quad (2.86)$$

which can alternatively be expressed as

$$M_{\text{dist}} = 2\pi \int_{r_0(R(t), t)}^1 \phi(r, 0) h(r, 0) r \, dr. \quad (2.87)$$

Note that, since all of the particles are initially within the bulk of the droplet, but are all eventually transferred to the distributed deposit, $M_{\text{dist}}(0) = 0$ and $M_{\text{dist}}(t_{\text{CA}}) = M_0$.

Following the approach of Freed-Brown [66] and D'Ambrosio *et al.* [84], the final density per unit area of the distributed deposit of particles on the substrate, denoted by $\phi_{\text{dist}} = \phi_{\text{dist}}(r)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0 \hat{\phi}_{\text{ref}}$, is given by

$$\phi_{\text{dist}}(R) = \phi(r_0(R, t), 0) h(r_0(R, t), 0) \frac{r_0(R, t)}{R} \frac{\partial(r_0(R, t))}{\partial R} \quad \text{for } 0 \leq R < 1, \quad (2.88)$$

and M_{dist} can be expressed in terms of ϕ_{dist} as

$$M_{\text{dist}} = 2\pi \int_{R(t)}^1 \phi_{\text{dist}}(r) r \, dr. \quad (2.89)$$

2.8.3 Particle Deposition in the SS Mode

In the SS mode, the droplet evolves in a CR phase with $R \equiv 1$ for $0 \leq t \leq t^*$ and then in a CA phase with $0 \leq R < 1$ for $t^* < t \leq t_{\text{SS}}$, resulting in the formation of a combined ring and distributed deposit comprising a ring deposit at $r = 1$ and a distributed deposit in $0 \leq r < 1$, as sketched in Figure 2.7(c). The mass of particles in the ring deposit is given by (2.83) and (2.84) for $0 \leq t \leq t^*$ and by $M_{\text{ring}} \equiv M_{\text{ring}}(t^*)$ for $t^* < t \leq t_{\text{SS}}$, and the mass of particles in the distributed deposit is given by $M_{\text{dist}} \equiv 0$

for $0 \leq t \leq t^*$ and by

$$M_{\text{dist}} = 2\pi \int_{t^*}^t \lim_{r \rightarrow R(t)^-} \phi(r, t) h(r, t) \left(\bar{u}(r, t) - \frac{dR}{dt} \right) r \, dt \quad (2.90)$$

for $t^* < t \leq t_{\text{SS}}$, the latter of which can alternatively be expressed as either

$$M_{\text{dist}} = 2\pi \int_{r_0(R(t), t)}^1 \phi(r, t^*) h(r, t^*) r \, dr \quad (2.91)$$

or (2.89), where ϕ_{dist} is given by

$$\phi_{\text{dist}}(R) = \phi(r_0(R, t), t^*) h(r_0(R, t), t^*) \frac{r_0(R, t)}{R} \frac{\partial(r_0(R, t))}{\partial R} \quad \text{for } 0 \leq R < 1. \quad (2.92)$$

2.8.4 Particle Deposition in the SJ Mode

In the SJ mode, the droplet evolves in a (theoretically infinite) sequence of CR phases with $R \equiv R_n$ for $t_{n-1} < t < t_n$ separated by a (theoretically infinite) sequence of instantaneous jump phases at $t = t_n$ ($n = 1, 2, 3, \dots$), resulting in the formation of a (theoretically infinite number of) ring deposits, as sketched in Figure 2.7(d). The mass of particles in the n th ($n = 1, 2, 3, \dots$) ring deposit, denoted by $M_{\text{ring}, n} = M_{\text{ring}, n}(t)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0 \hat{\phi}_{\text{ref}}$, is given by $M_{\text{ring}, n} \equiv 0$ for $0 \leq t < t_{n-1}$, and by

$$M_{\text{ring}, n} = 2\pi \int_{t_{n-1}}^t \lim_{r \rightarrow R_n^-} \phi(r, t) h(r, t) \bar{u}(r, t) r \, dt, \quad (2.93)$$

which can alternatively be expressed as

$$M_{\text{ring}, n} = 2\pi \int_{r_{0, n}(R_n, t)}^{R_n} \phi(r, t_{n-1}) h(r, t_{n-1}) r \, dr, \quad (2.94)$$

for $t_{n-1} < t < t_n$, and by $M_{\text{ring}, n} \equiv M_{\text{ring}, n}(t_n)$ for $t_n < t \leq t_{\text{SJ}}$. The total mass of particles in the multiple ring deposits, denoted by $M_{\text{rings}} = M_{\text{rings}}(t)$, is then determined by summing the masses of the particles in the ring deposits that have either been previously created or are still being created at time t .

Chapter 3

Evolution and Lifetime of a Thin Sessile Droplet

3.1 Overview

In this chapter, we determine the evolution, and hence the lifetime, of a thin sessile droplet on the three different porous substrates discussed in Chapter 2 in the CR, CA, SS, and SJ modes. In Section 3.2 we determine the evolution, and hence the lifetime, of a thin sessile droplet on an infinitely thick, isotropic, flooded, porous substrate. In Section 3.3 we determine the evolution, and hence the lifetime, of a thin sessile droplet on a finitely thick, anisotropic, initially dry, porous substrate. In Section 3.4 we determine the evolution, and hence the final depth, of the wetting front on a finitely thick, anisotropic, initially dry, porous substrate. In Section 3.5 we determine the evolution, and hence the lifetime, of a thin sessile droplet on a finitely thick, anisotropic, flooded, porous substrate.

3.2 An infinitely thick, isotropic, flooded, porous substrate

In this section, we determine the evolution, and hence the lifetime, of the droplet on an infinitely thick, isotropic, flooded, porous substrate undergoing simultaneous

evaporation and imbibition in the CR, CA, SS, and SJ modes.

Substituting the expressions for the local evaporation mass flux J_E given by (2.32) and the local imbibition mass flux J_I given by (2.44) into the evolution equation (2.23) and performing the integration, yields

$$\frac{d(\theta R^3)}{dt} = -\frac{16}{\pi}(\mathcal{E}R + 2\mathcal{I}\theta). \quad (3.1)$$

In situations in which evaporation dominates, it is most appropriate to choose $\hat{t}_{\text{ref}} = \hat{t}_{E,\text{ref}}$ given by (2.26) and $\hat{U}_{\text{ref}} = \hat{U}_{E,\text{ref}}$ and $\hat{J}_{\text{ref}} = \hat{J}_{E,\text{ref}}$ given by equation (2.25) in the non-dimensionalisation (2.2), and hence

$$\mathcal{E} = 1 \quad \text{and} \quad \mathcal{I} = \frac{\hat{U}_{I,\text{ref}}}{\hat{U}_{E,\text{ref}}} = \frac{\hat{J}_{I,\text{ref}}}{\hat{J}_{E,\text{ref}}} = \frac{\hat{t}_{E,\text{ref}}}{\hat{t}_{I,\text{ref}}} = \frac{\hat{\rho}\hat{\gamma}\hat{k}\hat{\theta}_0}{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})\hat{\mu}\hat{R}_0}. \quad (3.2)$$

On the other hand, in situations in which imbibition dominates, it is most appropriate to choose $\hat{t}_{\text{ref}} = \hat{t}_{I,\text{ref}}$ given by (2.36) and $\hat{U}_{\text{ref}} = \hat{U}_{I,\text{ref}}$ and $\hat{J}_{\text{ref}} = \hat{J}_{I,\text{ref}}$ given by equation (2.35) in the non-dimensionalisation (2.2), and hence

$$\mathcal{E} = \frac{\hat{U}_{E,\text{ref}}}{\hat{U}_{I,\text{ref}}} = \frac{\hat{J}_{E,\text{ref}}}{\hat{J}_{I,\text{ref}}} = \frac{\hat{t}_{I,\text{ref}}}{\hat{t}_{E,\text{ref}}} = \frac{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})\hat{\mu}\hat{R}_0}{\hat{\rho}\hat{\gamma}\hat{k}\hat{\theta}_0} \quad \text{and} \quad \mathcal{I} = 1. \quad (3.3)$$

For clarity of presentation, we leave $\hat{t}_{\text{ref}}$, $\hat{U}_{\text{ref}}$, and $\hat{J}_{\text{ref}}$ unspecified and retain both $\mathcal{E}$ and $\mathcal{I}$ in the general expressions given in the remainder of this thesis. In particular, taking this approach means that the results in the special case of a droplet undergoing pure evaporation expressed using the evaporation scaling leading to (3.2) can be obtained by setting $\mathcal{E} = 1$ and taking the limit $\mathcal{I} \rightarrow 0$, while the results in the special case of a droplet undergoing pure imbibition expressed using the imbibition scaling leading to (3.3) can be obtained by setting $\mathcal{I} = 1$ and taking the limit $\mathcal{E} \rightarrow 0$.

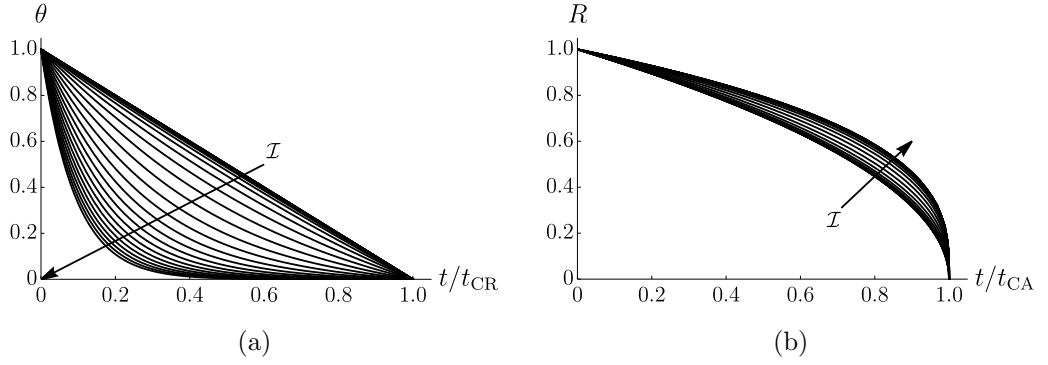


Figure 3.1: The evolutions of (a) θ for a droplet evolving in the CR mode given by (3.4) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of t/t_{CR} and (b) R for a droplet evolving in the CA mode given by (3.9) also for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of t/t_{CA} . The arrows indicate the directions of increasing $\mathcal{I}$.

3.2.1 Evolution and Lifetime in the CR Mode

Setting $R \equiv 1$ in (3.1) and solving for θ shows that a droplet undergoing simultaneous evaporation and imbibition in the CR mode evolves according to

$$R \equiv 1, \quad \theta = \frac{1}{2\mathcal{I}} \left[(\mathcal{E} + 2\mathcal{I}) \exp \left(-\frac{32\mathcal{I}}{\pi} t \right) - \mathcal{E} \right], \quad (3.4)$$

and so has lifetime

$$t_{\text{CR}} = \frac{\pi}{32\mathcal{I}} \log \left(\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E}} \right). \quad (3.5)$$

Figure 3.1(a) shows the evolution of θ given by (3.4) for a range of values of $\mathcal{I}$ plotted as a function of t/t_{CR} . In particular, (3.5) shows that, as expected, increasing the strength of evaporation and/or imbibition (i.e., increasing $\mathcal{E}$ and/or $\mathcal{I}$) shortens the lifetime of the droplet. In particular, a droplet undergoing pure evaporation evolves according to

$$R \equiv 1, \quad \theta = 1 - \frac{16}{\pi} t, \quad (3.6)$$

and so has lifetime $t_{\text{CR}} = t_{\text{CR,E}}$ given by

$$t_{\text{CR,E}} = \frac{\pi}{16} \quad (3.7)$$

(see, for example, Wilson & Duffy [237]), while a droplet undergoing pure imbibition evolves according to

$$R \equiv 1, \quad \theta = \exp\left(-\frac{32}{\pi}t\right) \rightarrow 0^+, \quad (3.8)$$

and so never completely imbibes, i.e., it has an infinitely long lifetime $t_{\text{CR}} = t_{\text{CR,I}} = \infty$. Physically, the qualitative difference in the behaviour of a droplet undergoing pure evaporation and pure imbibition in the CR mode arises because the global evaporation mass flux $F_{\text{E}} \equiv 4$ given by (2.33) remains constant as the droplet evolves because the contact line remains pinned. When combined with the droplet geometry, this leads to the finite lifetime (3.7) in the case of pure evaporation, whereas, since the leading-order pressure $p^{(0)} = 2\theta$ given by (2.9) tends to zero as the droplet evolves, the global imbibition mass flux $F_{\text{I}} \equiv 8\theta$ given by (2.45) also tends to zero. When combined with the droplet geometry, this leads to an infinitely long lifetime in the case of pure imbibition.

3.2.2 Evolution and Lifetime in the CA Mode

Setting $\theta \equiv 1$ in (3.1) and solving for R shows that a droplet undergoing simultaneous evaporation and imbibition in the CA mode evolves according to

$$\frac{3\pi}{32\mathcal{E}^3} \left[8\mathcal{I}^2 \log\left(\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E}R + 2\mathcal{I}}\right) + \mathcal{E}(1 - R)\{\mathcal{E}(1 + R) - 4\mathcal{I}\} \right] = t, \quad \theta \equiv 1, \quad (3.9)$$

and so has lifetime

$$t_{\text{CA}} = \frac{3\pi}{32\mathcal{E}^3} \left[8\mathcal{I}^2 \log\left(\frac{\mathcal{E} + 2\mathcal{I}}{2\mathcal{I}}\right) + \mathcal{E}(\mathcal{E} - 4\mathcal{I}) \right]. \quad (3.10)$$

Figure 3.1(b) shows the evolution of R given by (3.9) for a range of values of $\mathcal{I}$ plotted as a function of t/t_{CA} . In particular, (3.10) shows that, as in the CR mode, increasing

$\mathcal{E}$ and/or $\mathcal{I}$ shortens the lifetime of the droplet. In particular, a droplet undergoing pure evaporation in the CA mode evolves according to

$$R = \left(1 - \frac{32}{3\pi}t\right)^{1/2}, \quad \theta \equiv 1, \quad (3.11)$$

and so has lifetime $t_{\text{CA}} = t_{\text{CA,E}}$ given by

$$t_{\text{CA,E}} = \frac{3\pi}{32} = \frac{3}{2}t_{\text{CR,E}} \quad (3.12)$$

(see, for example, Wilson & Duffy [237]). Physically, the quantitative difference in the lifetime of a droplet undergoing pure evaporation in the CR and CA modes arises because the global evaporation mass flux, given by (2.33), remains constant in the CR mode, $F_{\text{E}} \equiv 4$, and tends to zero in the CA mode, $F_{\text{E}} \equiv 4R$, as the droplet evaporates. When combined with the droplet geometry, this reduction in F_{E} leads to an extended lifetime in the CA mode. A droplet undergoing pure imbibition in the CA mode evolves according to

$$R = \left(1 - \frac{32}{\pi}t\right)^{1/3}, \quad \theta \equiv 1, \quad (3.13)$$

and so has lifetime $t_{\text{CA}} = t_{\text{CA,I}}$ given by

$$t_{\text{CA,I}} = \frac{\pi}{32}. \quad (3.14)$$

According to (3.11) R^2 and $V^{2/3}$ are both linear in t , results that are often referred to in the literature as the “ d^2 law” and the “ $2/3$ law” of pure evaporation, respectively (see, for example, Wilson and D’Ambrosio [17]). Similarly, according to (3.11) R^3 and V are both linear in t , and so by analogy we could term these results the “ d^3 law” and the “ 1 law” of pure imbibition, respectively. Physically, the qualitative difference in the behaviour of a droplet undergoing pure imbibition in the CR and CA modes arises because the global imbibition mass flux, given by (2.45), tends to zero in the CR mode, $F_{\text{I}} \equiv 8\theta$, as the droplet imbibes. When combined with the droplet geometry, this leads

to an infinitely long lifetime. In the CA mode, by contrast, the leading-order pressure within the droplet, $p^{(0)} = 2/R$ given by (2.9), tends to infinity as the droplet imbibes and $F_I \equiv 8$ remains constant. When combined with the droplet geometry, this leads to the finite lifetime (3.14).

3.2.3 Evolution and Lifetime in the SS Mode

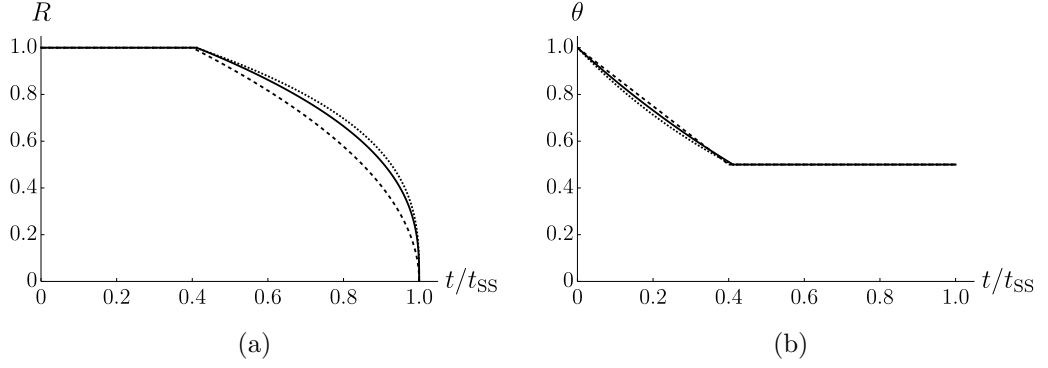


Figure 3.2: The evolutions of (a) R and (b) θ for a droplet evolving in the SS mode given by (3.16) and (3.4) with (3.15) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SS} when $\theta^* = 1/2$.

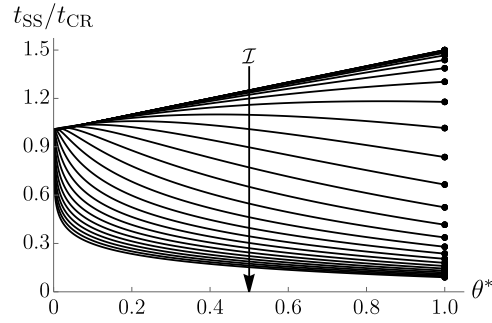


Figure 3.3: t_{SS}/t_{CR} given by (3.17) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of θ^* . The dots (•) indicate the values of t_{CA}/t_{CR} obtained when $\theta^* = 1$, and the arrow indicates the directions of increasing $\mathcal{I}$.

A droplet undergoing simultaneous evaporation and imbibition in the SS mode

evolves according to (3.4) in the CR phase for $0 \leq t \leq t^*$, where

$$t^* = \frac{\pi}{32\mathcal{I}} \log \left(\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E} + 2\mathcal{I}\theta^*} \right), \quad (3.15)$$

and according to

$$\frac{3\pi\theta^*}{32\mathcal{E}^3} \left[8\mathcal{I}^2\theta^{*2} \log \left(\frac{\mathcal{E} + 2\mathcal{I}\theta^*}{\mathcal{E}R + 2\mathcal{I}\theta^*} \right) + \mathcal{E}(1-R)\{\mathcal{E}(1+R) - 4\mathcal{I}\theta^*\} \right] = t - t^*, \quad \theta \equiv \theta^* \quad (3.16)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and so has lifetime

$$t_{\text{SS}} = \frac{\pi}{32\mathcal{E}^3\mathcal{I}} \left[\mathcal{E}^3 \log \left(\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E} + 2\mathcal{I}\theta^*} \right) + 3\mathcal{I}\theta^* \left\{ 8\mathcal{I}^2\theta^{*2} \log \left(\frac{\mathcal{E} + 2\mathcal{I}\theta^*}{2\mathcal{I}\theta^*} \right) + \mathcal{E}(\mathcal{E} - 4\mathcal{I}\theta^*) \right\} \right]. \quad (3.17)$$

Figure 3.2 shows the evolutions of R and θ given by (3.16) and (3.4) for pure evaporation (dashed line), simultaneous evaporation and imbibition (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SS} when $\theta^* = 1/2$. Figure 3.3 shows $t_{\text{SS}}/t_{\text{CR}}$ given by (3.17) for a range of values of $\mathcal{I}$ plotted as a function of θ^* . In particular, Figure 3.3 illustrates that t_{SS} is, in general, a non-monotonic function of θ^* , and that t_{SS} does not, as might have naively been expected, always lie between t_{CR} and t_{CA} . The non-monotonicity arises from the opposing trends in the pure evaporation and imbibition problems, respectively. In particular, a droplet undergoing pure evaporation evolves according to (3.6) in the CR phase for $0 \leq t \leq t^*$, where $t^* = t_{\text{E}}^*$ is given by

$$t_{\text{E}}^* = \frac{\pi(1 - \theta^*)}{16}, \quad (3.18)$$

and according to

$$R = \left[1 - \frac{32}{3\pi\theta^*} (t - t_{\text{E}}^*) \right]^{1/2}, \quad \theta \equiv \theta^* \quad (3.19)$$

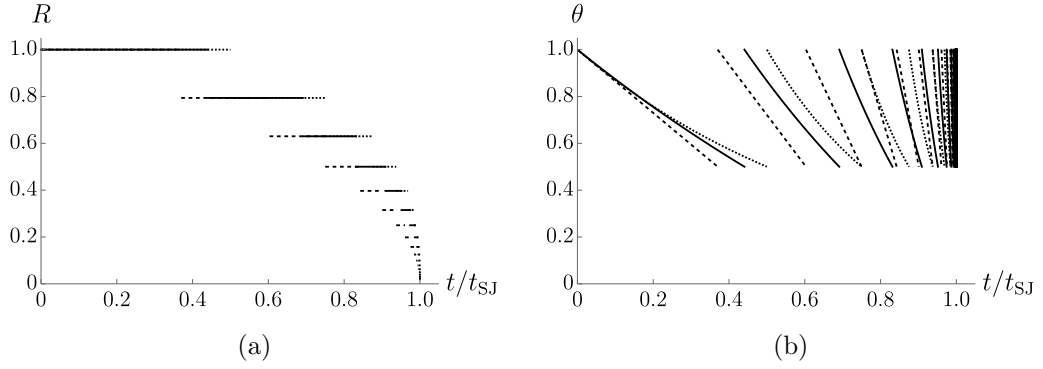


Figure 3.4: The evolutions of (a) R and (b) θ for a droplet evolving in the SJ mode are given by (3.24) with (3.26) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SJ} when $\theta_{\min} = 1/2$.

in the CA phase for $t^* < t \leq t_{SS}$, and so has lifetime $t_{SS} = t_{SS,E}$ given by

$$t_{SS,E} = \frac{\pi(2 + \theta^*)}{32} \quad (3.20)$$

(see, for example, Wilson & Duffy [237]). On the other hand, a droplet undergoing pure imbibition evolves according to (3.8) in the CR phase for $0 \leq t \leq t^*$, where $t^* = t_I^*$ is given by

$$t_I^* = \frac{\pi}{32}(-\log \theta^*), \quad (3.21)$$

and according to

$$R = \left[1 - \frac{32}{\pi}(t - t_I^*) \right]^{1/3}, \quad \theta \equiv \theta^* \quad (3.22)$$

in the CA phase for $t^* < t \leq t_{SS}$, and so has lifetime $t_{SS} = t_{SS,I}$ given by

$$t_{SS,I} = \frac{\pi}{32}(1 - \log \theta^*). \quad (3.23)$$

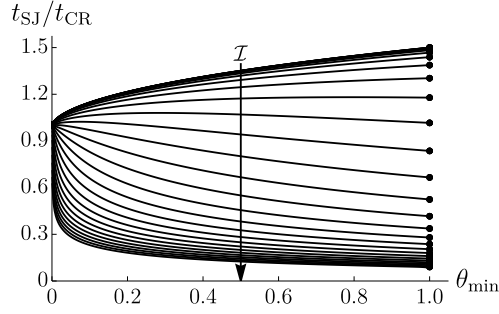


Figure 3.5: $t_{\text{SJ}}/t_{\text{CR}}$ given by (3.27) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of $\theta_{\min}$. The dots ($\bullet$) indicate the values of $t_{\text{CA}}/t_{\text{CR}}$ obtained in the limit $\theta_{\min} \rightarrow \theta_{\max}^- = 1^-$, and the arrow indicates the directions of increasing $\mathcal{I}$.

3.2.4 Evolution and Lifetime in the SJ Mode

A droplet undergoing simultaneous evaporation and imbibition in the SJ mode evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \left(\theta_{\max} + \frac{\mathcal{E} R_n}{2\mathcal{I}} \right) \exp \left[-\frac{32\mathcal{I}}{\pi R_n^3} (t - t_{n-1}) \right] - \frac{\mathcal{E} R_n}{2\mathcal{I}} \quad (3.24)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), the duration of the n th CR phase, denoted by $\delta t_n = t_n - t_{n-1}$, is given by

$$\delta t_n = \frac{\pi}{32\mathcal{I}} \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{n-1} \log \left[\frac{\mathcal{E} \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3} + 2\mathcal{I}\theta_{\max}}{\mathcal{E} \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3} + 2\mathcal{I}\theta_{\min}} \right], \quad (3.25)$$

the time at which the n th CR phase ends, namely $t = t_n$, is given by

$$t_n = \sum_{i=1}^n \delta t_i, \quad (3.26)$$

and so has lifetime

$$t_{\text{SJ}} = \lim_{n \rightarrow \infty} t_n, \quad (3.27)$$

which must, in general, be evaluated numerically, which was implemented using Mathematica [238]. Figure 3.4 shows the evolutions of R and θ given by (3.24) with (3.26) for pure evaporation (dashed line), simultaneous evaporation and imbibition (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SJ} when $\theta_{\min} = 1/2$. Figure 3.5 shows $t_{\text{SJ}}/t_{\text{CR}}$ given by (3.27) for a range of values of $\mathcal{I}$ plotted as a function of $\theta_{\min}$. In particular, Figure 3.5 illustrates, similarly to the variation of t_{SS} with θ^* in the SS mode shown in Figure 3.3, that t_{SJ} is, in general, a non-monotonic function of $\theta_{\min}$, and that t_{SJ} does not, as might have naively been expected, always lie between t_{CR} and t_{CA} . In particular, a droplet undergoing pure evaporation evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \theta_{\max} - \frac{16}{\pi R_n^2} (t - t_{n-1}) \quad (3.28)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), with

$$\delta t_{n,E} = \frac{\pi}{16} (\theta_{\max} - \theta_{\min}) \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2(n-1)/3} \quad (3.29)$$

and

$$t_{n,E} = \frac{\pi (\theta_{\max} - \theta_{\min})}{16} \left[\frac{1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2n/3}}{1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2/3}} \right], \quad (3.30)$$

and so has lifetime $t_{\text{SJ}} = t_{\text{SJ},E}$ given by

$$t_{\text{SJ},E} = \frac{\pi (\theta_{\max} - \theta_{\min})}{16} \frac{\theta_{\max}^{2/3}}{\theta_{\max}^{2/3} - \theta_{\min}^{2/3}} \quad (3.31)$$

(see, for example, Wilson & Duffy [237]). On the other hand, a droplet undergoing pure imbibition evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \theta_{\max} \exp \left(-\frac{32}{\pi R_n^3} (t - t_{n-1}) \right) \quad (3.32)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), with

$$\delta t_{n,I} = \frac{\pi}{32} \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{n-1} \log \left(\frac{\theta_{\max}}{\theta_{\min}} \right) \quad (3.33)$$

and

$$t_{n,I} = \frac{\pi}{32} \frac{\left[1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^n \right]}{\left[1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right) \right]} \log \left(\frac{\theta_{\max}}{\theta_{\min}} \right), \quad (3.34)$$

and so has lifetime $t_{SJ} = t_{SJ,I}$ given by

$$t_{SJ,I} = \frac{\pi \theta_{\max}}{32(\theta_{\max} - \theta_{\min})} \log \left(\frac{\theta_{\max}}{\theta_{\min}} \right). \quad (3.35)$$

3.3 A finitely thick, anisotropic, initially dry, porous substrate

In this section, we determine the evolution, and hence the lifetime, of the droplet on a finitely thick, anisotropic, initially dry, porous substrate undergoing simultaneous evaporation and imbibition in the CR, CA, SS, and SJ modes. In particular, the evolution, and hence the lifetime, of a droplet undergoing pure evaporation in the CR, CA, SS, and SJ modes are given in Sections 3.2.1, 3.2.2, 3.2.3, and 3.2.4, respectively.

Substituting the expressions for the local evaporation mass flux J_E given by (2.32) and the local imbibition mass flux J_I given by (2.57) into the evolution equation (2.23) and performing the integration, yields

$$\frac{d(\theta R^3)}{dt} = -2R \left[\frac{8\mathcal{E}}{\pi} + R \left(\frac{2\mathcal{I}}{t} \right)^{1/2} \right]. \quad (3.36)$$

In situations in which evaporation dominates, as discussed in Section 3.2,

$$\mathcal{E} = 1 \quad \text{and} \quad \mathcal{I} = \frac{\hat{U}_{I,\text{ref}}}{\hat{U}_{E,\text{ref}}} = \frac{\hat{J}_{I,\text{ref}}}{\hat{J}_{E,\text{ref}}} = \frac{\hat{t}_{E,\text{ref}}}{\hat{t}_{I,\text{ref}}} = \frac{\hat{\rho} \varphi \hat{k} \hat{P}_c}{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})}. \quad (3.37)$$

On the other hand, in situations in which imbibition dominates, as also discussed in

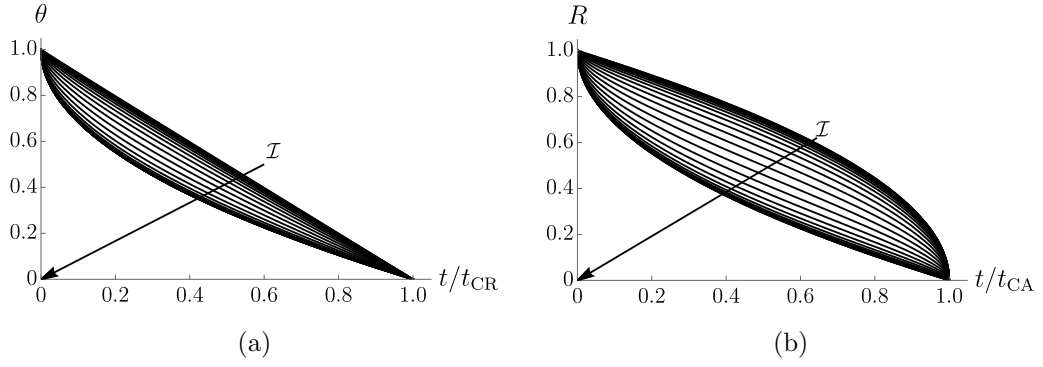


Figure 3.6: The evolutions of (a) θ for a droplet evolving in the CR mode given by (3.39) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) plotted as a function of t/t_{CR} and (b) R for a droplet evolving in the CA mode given by (3.43) also for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) plotted as a function of t/t_{CA} . The arrows indicate the directions of increasing $\mathcal{I}$.

Section 3.2,

$$\mathcal{E} = \frac{\hat{U}_{\text{E,ref}}}{\hat{U}_{\text{I,ref}}} = \frac{\hat{J}_{\text{E,ref}}}{\hat{J}_{\text{I,ref}}} = \frac{\hat{t}_{\text{I,ref}}}{\hat{t}_{\text{E,ref}}} = \frac{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})}{\hat{\rho}\varphi\hat{k}\hat{P}_{\text{c}}} \quad \text{and} \quad \mathcal{I} = 1. \quad (3.38)$$

3.3.1 Evolution and Lifetime in the CR Mode

Setting $R \equiv 1$ in (3.36) and solving for θ shows that a droplet undergoing simultaneous evaporation and imbibition in the CR mode evolves according to

$$R \equiv 1, \quad \theta = 1 - \frac{16\mathcal{E}}{\pi}t - 4(2\mathcal{I}t)^{1/2}, \quad (3.39)$$

and so has lifetime

$$t_{\text{CR}} = \frac{\pi \left[\pi\mathcal{I} \left(1 - \left\{ 1 + \frac{2\mathcal{E}}{\pi\mathcal{I}} \right\}^{1/2} \right) + \mathcal{E} \right]}{16\mathcal{E}^2}. \quad (3.40)$$

Figure 3.6(a) shows the evolution of θ given by (3.39) for a range of values of $\mathcal{I}$ plotted as a function of t/t_{CR} . In particular, (3.40) shows that, as expected, increasing the strength of evaporation and/or imbibition (i.e., increasing $\mathcal{E}$ and/or $\mathcal{I}$) shortens the lifetime of the droplet. In particular, a droplet undergoing pure imbibition evolves

Symbol	$\hat{R}_0$ (mm)	$\hat{\theta}_0$ (°)	$\hat{t}_{\text{E,ref}}$ (s)	$\hat{t}_{\text{I,fit}}$ (s)	$\hat{t}_{\text{CR,fit}}$ (s)	R^2	$\mathcal{E}$	$1 - \frac{\hat{t}_{\text{CR,fit}}}{\hat{t}_{\text{CR,I}}}$ (%)
●	1.64	19.70	2444.40	78.14	2.42	0.99	0.03	0.90
■	1.86	16.36	2611.13	223.24	6.79	0.99	0.09	2.67
▲	2.03	15.52	2950.55	404.66	12.12	0.91	0.14	4.16

Table 3.1: The values of $\hat{R}_0$, $\hat{\theta}_0$, $\hat{t}_{\text{E,ref}}$, $\hat{t}_{\text{I,fit}}$, $\hat{t}_{\text{CR,fit}}$, R^2 , $\mathcal{E}$, and $1 - \hat{t}_{\text{CR,fit}}/\hat{t}_{\text{CR,I}}$ used in our analysis, and based on the experimental results of Li *et al.* [6].

according to

$$R \equiv 1, \quad \theta = 1 - 4(2t)^{1/2}, \quad (3.41)$$

and so has lifetime $t_{\text{CR}} = t_{\text{CR,I}}$ given by

$$t_{\text{CR,I}} = \frac{1}{32} \quad (3.42)$$

(see, for example, Denesuk *et al.* [118] and Middleman [127]). We note that the dimensional solutions for the evolution, and hence the lifetime, as determined by Denesuk *et al.* [118] and Middleman [127] are recovered by substituting $\hat{k}$ and $\hat{P}_c$ given by (2.46) into (2.49). From equation (3.40) we infer that the lifetime is only weakly sensitive to small evaporation in an imbibition-dominated evolution, with $t_{\text{CR}} \sim 1/32 - \mathcal{E}/(32\pi)$ as $\mathcal{E} \rightarrow 0$ when $\mathcal{I} = 1$. In contrast, for an evaporation-dominated evolution the lifetime is strongly affected by even weak imbibition, with $t_{\text{CR}} \sim \pi/16 - \pi^{3/2}(2\mathcal{I})^{1/2}/16$ as $\mathcal{I} \rightarrow 0$ when $\mathcal{E} = 1$. Hence, weak evaporation produces only a small correction to the lifetime, whereas weak imbibition produces a comparatively large correction to the lifetime.

3.3.2 Experimental Comparisons in the CR Mode: Imbibition Dominates

In contrast to the situation described in Section 3.2, several authors have experimentally investigated the simultaneous evaporation and imbibition of a droplet on a finitely thick, anisotropic, initially dry, porous substrate. In order to verify and validate equation (3.39) when imbibition dominates, we compare the predictions of the present model

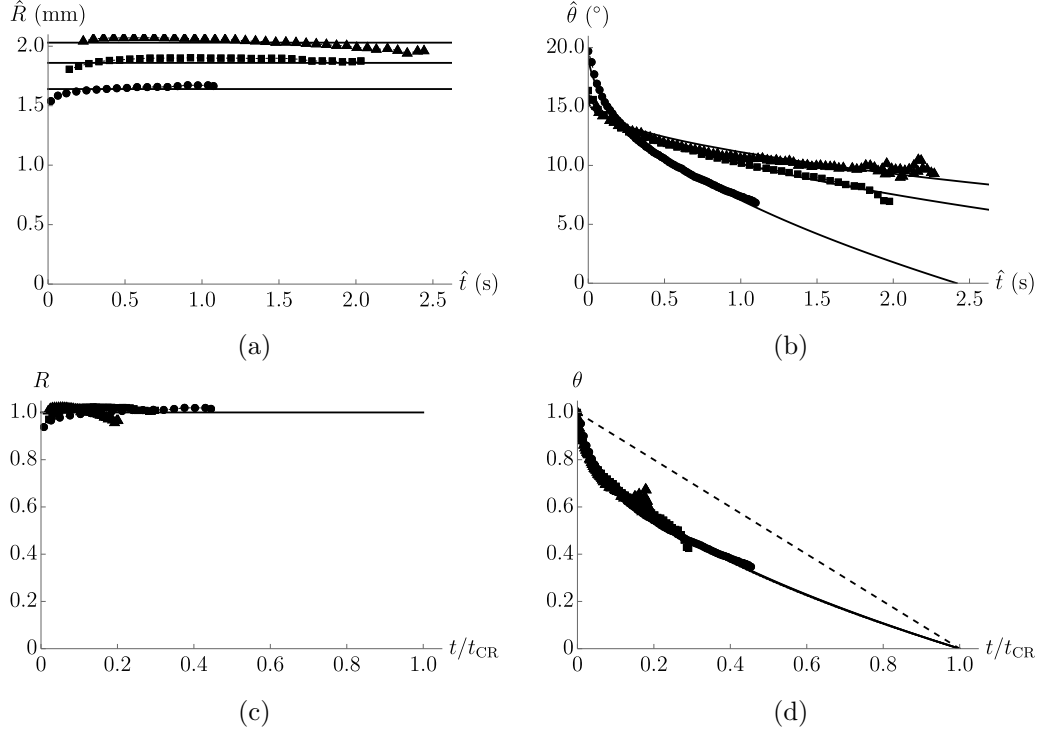


Figure 3.7: Comparison of the evolution of droplets in the CR mode: (a) the contact radius $\hat{R}$ and the contact angle $\hat{\theta}$ as a function of $\hat{t}$, (c) the contact radius $R \equiv 1$ (solid line) as a function of t/t_{CR} and (d) θ from (3.39) with $\mathcal{I} = 1$ and $\mathcal{E}$ from Table 3.1 (solid lines), together with pure evaporation (dashed) and pure imbibition (dotted), plotted as functions of t/t_{CR} . The symbols denote the corresponding experimental results of Li *et al.* [6].

with the results of the experimental investigation of Li *et al.* [6], as discussed in Section 2.5. These authors measured the evolutions of R and θ of water droplets with increasing initial volume. The experiments were carried out at a temperature of $\hat{T} = 22^\circ\text{C}$ and the porosity of the substrate was reported to be $\varphi = 0.33$. The constant density, viscosity, diffusion coefficient, saturation concentration, and far-field concentration of a water droplet as given by Li *et al.* [6] are $\hat{\rho} = 1000 \text{ kg m}^{-3}$, $\hat{\mu} = 10^{-3} \text{ Pa s}$, $\hat{D} = 26.1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, $\hat{c}_{\text{sat}} = 2.23 \times 10^{-2} \text{ kg m}^{-3}$, and $\hat{c}_{\infty} = 0.78 \times 10^{-2} \text{ kg m}^{-3}$, respectively. The initial values $\hat{R}_0$ and $\hat{\theta}_0$ are given in Table 3.1.

The evolution of R and θ , respectively, for the droplets considered by Li *et al.* [6] are shown in Figure 3.7. From the reported parameter values, we determine the evaporation timescale $\hat{t}_{E,\text{ref}}$, and then obtain a fitted value for $\mathcal{I}$ by applying the `FindFit` function

Symbol	$\hat{R}_0$ (mm)	$\hat{\theta}_0$ (°)	$\hat{t}_{E,\text{ref}}$ (10^3 s)	$\hat{t}_{I,\text{fit}}$ (10^3 s)	$\hat{t}_{CR,\text{fit}}$ (10^3 s)	R^2	$\mathcal{I}$	$1 - \frac{\hat{t}_{CR,\text{fit}}}{\hat{t}_{CR,E}}$ (%)
●	1.10	57.87	33.05	857.10	3.99	0.99	0.04	38.51
■	1.03	56.72	60.25	1207.09	6.81	0.98	0.05	42.43
▲	0.95	59.60	284.77	2521.53	24.64	0.98	0.11	55.93

Table 3.2: The values of $\hat{R}_0$, $\hat{\theta}_0$, $\hat{t}_{E,\text{ref}}$, $\hat{t}_{I,\text{fit}}$, $\hat{t}_{CR,\text{fit}}$, R^2 , $\mathcal{I}$, and $1 - \hat{t}_{CR,\text{fit}}/\hat{t}_{CR,E}$ used in our analysis, and based on the experimental results of Willis *et al.* [10].

in Mathematica [238] to (3.39). From this fitted $\mathcal{I}$ value, we calculate theoretical values for the imbibition timescale $\hat{t}_{I,\text{fit}}$ and droplet lifetime $\hat{t}_{CR,\text{fit}}$. This yields $\hat{t}_{E,\text{ref}}$, $\mathcal{I}$, $\hat{t}_{I,\text{fit}}$, and $\hat{t}_{CR,\text{fit}}$, together with the associated coefficient of determination values, denoted by R^2 , all of which are given in Table 3.1 for which the R^2 values are all close to unity.

The predictions for the evolution of the present model (i.e., equation (3.39)) shows good quantitative agreement with the experimental data, as indicated by the R^2 values in Table 3.1. Under the experimental conditions studied by Li *et al.* [6], which correspond to a relatively small evaporation number $\mathcal{E}$, the predicted droplet lifetime for simultaneous evaporation and imbibition is approximately 1–4% shorter than that for pure imbibition.

3.3.3 Experimental Comparisons in the CR Mode: Evaporation Dominates

In order to verify and validate (3.39) when evaporation dominates, we compare the predictions of the present model with the results of the experimental investigations of Willis *et al.* [10] and Richards *et al.* [11], as discussed in Section 3.3.2. Willis *et al.* [10] measured the evolutions of R and θ of HD droplets at temperatures of $\hat{T} = 20, 40$, and 50 °C. The constant density, diffusion coefficient, saturation concentration, and far-field concentration of HD droplets as given by Willis *et al.* [10] are $\hat{\rho} = 1274, 1253$, and 1242 kg m $^{-3}$, $\hat{D} = 7.0, 7.8$, and 8.2×10^{-6} m 2 s $^{-1}$, $\hat{c}_{\text{sat}} = 0.0006, 0.0028$, and 0.0056 kg m $^{-3}$, and $\hat{c}_{\infty} = 0$ kg m $^{-3}$ at each temperature, respectively. The initial values $\hat{R}_0$ and $\hat{\theta}_0$ are given in Table 3.2.

The evolution of θ for the droplets investigated by Willis *et al.* [10] are shown in

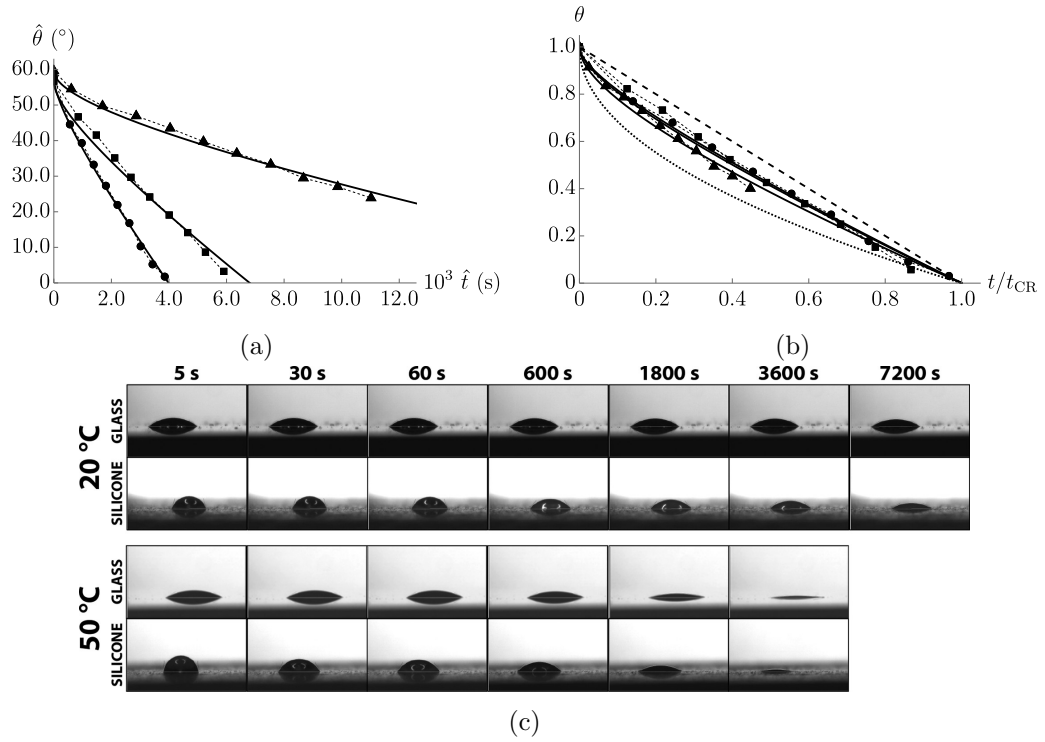


Figure 3.8: Comparison of the evolution of droplets in the CR mode: (a) θ from the dimensional form of (3.39) with $\hat{t}_{E,ref}$ and $\hat{t}_{I,fit}$ from Table 3.2 (solid lines) as a function of $\hat{t}$, (b) θ from (3.39) with $\mathcal{E} = 1$ and $\mathcal{I}$ from Table 3.2 (solid lines), together with pure evaporation (dashed line) and pure imbibition (dotted line), plotted as functions of t/t_{CR} , and (c) experimental images of a droplet evaporating on a solid glass substrate and simultaneously evaporating and imbibing on a porous silicone substrate. Reproduced from Figure 2 of Willis *et al.* [10] with permission, Copyright 2012, from the American Chemical Society. In (a,b) the symbols denote the corresponding experimental results of Willis *et al.* [10].

Symbol	$\hat{R}_0$ (mm)	$\hat{\theta}_0$ (°)	$\hat{t}_{E,\text{ref}}$ (s)	$\hat{t}_{I,\text{fit}}$ (10^3s)	$\hat{t}_{CR,\text{fit}}$ (s)	R^2	$\mathcal{I}$	$1 - \frac{\hat{t}_{CR,\text{fit}}}{\hat{t}_{CR,E}}$ (%)
●	1.22	40.00	458.10	154.02	78.46	0.99	0.003	12.77
■	1.33	31.00	1369.78	468.52	234.89	0.99	0.003	12.67

Table 3.3: The values of $\hat{R}_0$, $\hat{\theta}_0$, $\hat{t}_{E,\text{ref}}$, $\hat{t}_{I,\text{fit}}$, $\hat{t}_{CR,\text{fit}}$, R^2 , $\mathcal{I}$, and $1 - \hat{t}_{CR,\text{fit}}/\hat{t}_{CR,E}$ used in our analysis, and based on the experimental results of Richards *et al.* [11].

Figure 3.8. Figure 3.8(c) shows side-view images which show both a droplet undergoing pure evaporation on a solid glass substrate and one undergoing simultaneous evaporation and imbibition on a porous silicone substrate. From the reported parameter values, we determine $\hat{t}_{E,\text{ref}}$ and obtain a fitted value for $\mathcal{I}$ from (3.39), following the same approach outlined in Section 3.3.2 for the analysis of Li *et al.* [6]. This approach yields $\hat{t}_{E,\text{ref}}$, $\mathcal{I}$, $\hat{t}_{I,\text{fit}}$, and $\hat{t}_{CR,\text{fit}}$, together with the associated R^2 values, all of which are given in Table 3.2.

The predictions for the evolution of the present model show good quantitative agreement with the experimental data, as indicated by the R^2 values. Under the experimental conditions of Willis *et al.* [10], which correspond to a relatively small $\mathcal{I}$, the predicted droplet lifetime for simultaneous evaporation and imbibition is 39–56% shorter than that for pure evaporation.

Richards *et al.* [11] measured the evolution of the contact angle of trichloroethylene and tetrachloroethylene droplets. The experiments were carried out at a temperature of $\hat{T} = 22$ °C. The constant density, diffusion coefficient, saturation concentration, and far-field concentration of trichloroethylene and tetrachloroethylene droplets as given by Richards *et al.* [11] are $\hat{\rho} = 1460$ and 1620 kg m⁻³, $\hat{D} = 8.3$ and 7.7×10^{-6} m² s⁻¹, $\hat{c}_{\text{sat}} = 0.399$ and 0.147 kg m⁻³, and $\hat{c}_{\infty} = 0$ kg m⁻³, respectively. The initial values $\hat{R}_0$ and $\hat{\theta}_0$ are given in Table 3.3 for which the R^2 values are all close to unity.

The evolution of θ for the droplets investigated by Richards *et al.* [11] is shown in Figure 3.9. From the reported parameter values, we determine $\hat{t}_{E,\text{ref}}$ and obtain a fitted value for $\mathcal{I}$ from (3.39), following the same approach outlined above for the analysis of Li *et al.* [6]. This procedure yields $\hat{t}_{E,\text{ref}}$, $\mathcal{I}$, $\hat{t}_{I,\text{fit}}$, and $\hat{t}_{CR,\text{fit}}$, together with the associated R^2 values, all of which are given in Table 3.3 for which the R^2 values are

all close to unity.

The results show good quantitative agreement between the experimental data and (3.39), as indicated by the R^2 values. Under the experimental conditions of Richards *et al.* [11], which correspond to a very small $\mathcal{I}$, the predicted droplet lifetime for simultaneous evaporation and imbibition is approximately 13% shorter than that for pure evaporation.

Assuming that the flow within the porous substrates experimentally investigated by Li *et al.* [6], Willis *et al.* [10], and Richards *et al.* [11] can be idealised as Hagen–Poiseuille flow, we substitute the permeability and capillary pressure given by equation (2.46) into the characteristic imbibition timescale (2.49), giving $\hat{a} = 4\hat{\mu}\hat{\theta}_0^2\hat{R}_0^2/(\phi^2\hat{t}_{\mathcal{I},\text{fit}}\hat{\gamma}\cos\hat{\alpha})$. Assuming that $\cos\hat{\alpha} \approx 1$ and applying this procedure to the Li *et al.* [6] and Willis *et al.* [10] data yields pore radii of order 1 nm. Li *et al.* [6] report that their substrate is nanoporous, and Willis *et al.* [10] do not provide a characteristic pore size, so the inferred value cannot be compared directly with their measurements. In contrast, the Richards *et al.* [11] data imply a pore radius of order 10^{-2} nm, which is several orders of magnitude smaller than typical pore sizes reported for nanoporous polymeric materials. This discrepancy suggests that the simple Hagen–Poiseuille model does not capture the imbibition behaviour in the Richards *et al.* [11] experiments, while remaining appropriate for the other two porous substrates. Nanoporous polymeric materials commonly exhibit pore sizes well below 200 nm (see, for example, Notario *et al.* [citation no]), so the inferred nanometre-scale values for the Li *et al.* [6] and Willis *et al.* [10] data are at least qualitatively plausible.

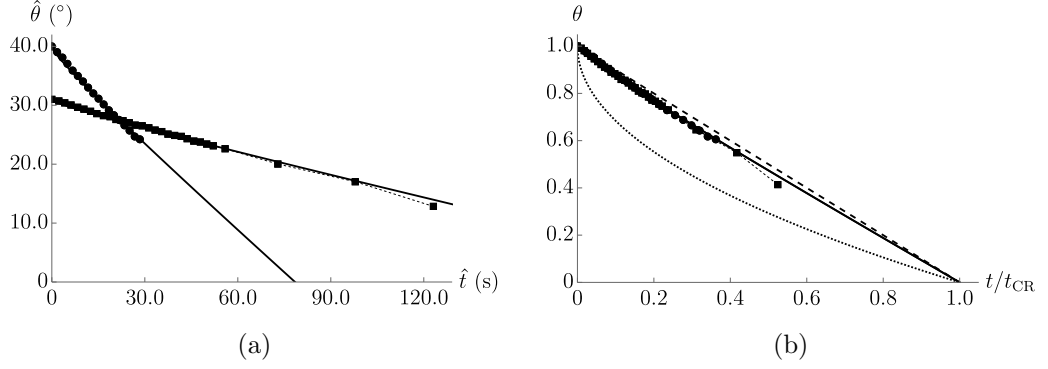


Figure 3.9: Comparison of the evolution of droplets in the CR mode: (a) θ from the dimensional form of (3.39) with $\hat{t}_{E,ref}$ and $\hat{t}_{I,fit}$ from Table 3.3 (solid lines) as a function of $\hat{t}$ (s), and (b) θ from (3.39) with $\mathcal{E} = 1$ and $\mathcal{I}$ from Table 3.3 (solid lines), together with pure evaporation (dashed line) and pure imbibition (dotted line), plotted as functions of t/t_{CR} . In (a,b), model predictions are compared with the experimental results (markers) of Richards *et al.* [11].

3.3.4 Evolution and Lifetime in the CA Mode

Setting $\theta \equiv 1$ in (3.36) and solving for R shows that a droplet undergoing simultaneous evaporation and imbibition in the CA mode evolves according to

$$\log \left[\frac{32\mathcal{E}}{3\pi}t + \frac{4}{3}(2\mathcal{I}t)^{1/2}R + R^2 \right] + \frac{2 \tanh^{-1} \left[\frac{1 + \frac{3R}{2(2\mathcal{I}t)^{1/2}}}{\left(1 - \frac{12\mathcal{E}}{\pi\mathcal{I}}\right)^{1/2}} \right]}{\left(1 - \frac{12\mathcal{E}}{\pi\mathcal{I}}\right)^{1/2}} + \frac{\pi}{\left(\frac{12\mathcal{E}}{\pi\mathcal{I}} - 1\right)^{1/2}} = 0, \quad \theta \equiv 1, \quad (3.43)$$

and so has lifetime

$$t_{CA} = \frac{3\pi}{32\mathcal{E}} \left[\frac{\pi\mathcal{I} \left(1 - \left\{1 - \frac{12\mathcal{E}}{\pi\mathcal{I}}\right\}^{1/2}\right)}{6\mathcal{E}} - 1 \right] \left(1 - \frac{12\mathcal{E}}{\pi\mathcal{I}}\right)^{-1/2}. \quad (3.44)$$

Figure 3.6(b) shows the evolution of R given by (3.43) for a range of values of $\mathcal{I}$ plotted as a function of t/t_{CA} . In particular, (3.44) shows that, as in the CR mode, increasing $\mathcal{E}$ and/or $\mathcal{I}$ shortens the lifetime of the droplet. In particular, a droplet undergoing

pure imbibition in the CA mode evolves according to

$$R = 1 - \frac{4}{3}(2t)^{1/2}, \quad \theta \equiv 1, \quad (3.45)$$

and so has lifetime $t_{\text{CA}} = t_{\text{CA,I}}$ given by

$$t_{\text{CA,I}} = \frac{9}{32} = 9t_{\text{CR,I}} \quad (3.46)$$

(see, for example, Denesuk *et al.* [118]). Physically, the quantitative difference in the lifetime of a droplet undergoing pure imbibition in the CR and CA mode arises because the global imbibition mass flux, given by (2.58), tends to $4/\pi$ in the CR mode, $F_I \equiv 4\pi/(1 - \theta)$, and tends to zero in the CA mode, $F_I \equiv 4\pi R^2/(3(1 - R))$, as the droplet imbibes. When combined with the droplet geometry, this reduction in F_I leads to an extended lifetime in the CA mode.

3.3.5 Evolution and Lifetime in the SS Mode

A droplet undergoing simultaneous evaporation and imbibition in the SS mode evolves according to (3.39) in the CR phase for $0 \leq t \leq t^*$, where

$$t^* = \frac{\pi^2 \mathcal{I} \beta}{16 \mathcal{E}^2}, \quad (3.47)$$

and we have introduced the notation

$$\beta = 1 - \left[1 + \frac{2\mathcal{E}(1 - \theta^*)}{\pi \mathcal{I}} \right]^{1/2} + \frac{\mathcal{E}(1 - \theta^*)}{\pi \mathcal{I}}, \quad (3.48)$$

and according to

$$\begin{aligned} & 2 \left[\tanh^{-1} \left(\frac{1 + \frac{3R\theta^*}{2(2\mathcal{I}t)^{1/2}}}{\left\{ 1 - \frac{12\mathcal{E}\theta^*}{\pi \mathcal{I}} \right\}^{1/2}} \right) - \tanh^{-1} \left(\frac{1 + \frac{3\theta^*}{2(2\mathcal{I}t^*)^{1/2}}}{\left\{ 1 - \frac{12\mathcal{E}\theta^*}{\pi \mathcal{I}} \right\}^{1/2}} \right) \right] \\ & + \left(1 - \frac{12\mathcal{E}\theta^*}{\pi \mathcal{I}} \right)^{1/2} \log \left[\frac{\mathcal{E}t + \pi R \left(\frac{(\mathcal{I}t)^{1/2}}{4(2)^{1/2}} + \frac{3R\theta^*}{32} \right)}{\mathcal{E}t^* + \pi \left(\frac{(\mathcal{I}t^*)^{1/2}}{4(2)^{1/2}} + \frac{3\theta^*}{32} \right)} \right] = 0, \quad \theta \equiv \theta^* \end{aligned} \quad (3.49)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and so has lifetime

$$t_{\text{SS}} = \frac{\pi^2 \mathcal{I}}{16 \mathcal{E}^2} \left[\beta + \left(\frac{\beta}{2} \right)^{1/2} + \frac{\theta^* (1 + \mathcal{E})}{\pi \mathcal{I}} \right] \left[\frac{\beta + \frac{\beta^{1/2} \left(1 - \left\{ 1 - \frac{12 \mathcal{E} \theta^*}{\pi \mathcal{I}} \right\}^{1/2} \right)}{2^{3/2}}}{\beta + \frac{\beta^{1/2} \left(1 + \left\{ 1 - \frac{12 \mathcal{E} \theta^*}{\pi \mathcal{I}} \right\}^{1/2} \right)}{2^{3/2}}} \right] \left(1 - \frac{12 \mathcal{E} \theta^*}{\pi \mathcal{I}} \right)^{-1/2}. \quad (3.50)$$

Figure 3.10 shows the evolutions of R and θ given by (3.49) and (3.39) with (3.47) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SS} when $\theta^* = 1/2$. Figure 3.11 shows $t_{\text{SS}}/t_{\text{CR}}$ given by (3.50) for a range of values of $\mathcal{I}$ plotted as a function of θ^* . In particular, Figure 3.11 illustrates that, in contrast to the simultaneous evaporation and imbibition of a droplet on an infinitely thick, isotropic, flooded, porous substrate, t_{SS} is a monotonic function of θ^* , and that t_{SS} does always lie between t_{CR} and t_{CA} . In particular, a droplet undergoing pure imbibition in the SS mode evolves according to (3.41) in the CR phase for $0 \leq t \leq t^*$, where $t^* = t_{\text{I}}^*$ is given by

$$t_{\text{I}}^* = \frac{(1 - \theta^*)^2}{32}, \quad (3.51)$$

and according to

$$R = 1 - \frac{4}{3\theta^*} \left[2^{1/2} \left(t^{1/2} - t_{\text{I}}^{*1/2} \right) \right], \quad \theta \equiv \theta^* \quad (3.52)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and so has lifetime $t_{\text{SS}} = t_{\text{SS,I}}$ given by

$$t_{\text{SS,I}} = \frac{(1 + 2\theta^*)^2}{32}. \quad (3.53)$$

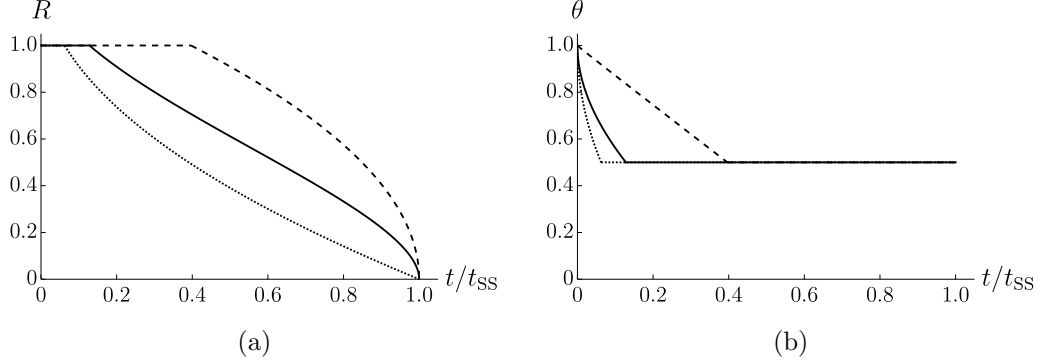


Figure 3.10: The evolutions of (a) R and (b) θ for a droplet evolving in the SS mode given by (3.49) and (3.39) with (3.47) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SS} when $\theta^* = 1/2$.

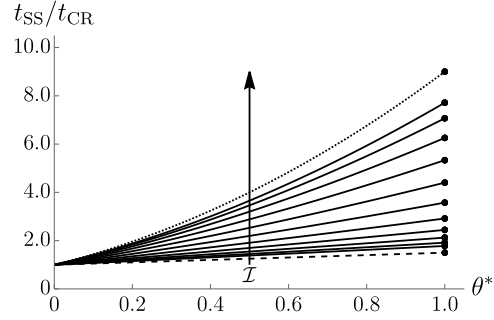


Figure 3.11: t_{SS}/t_{CR} given by (3.50) for pure evaporation (dashed line), simultaneous evaporation $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) (solid lines), and pure imbibition (dotted line) plotted as functions of θ^* . The dots (•) indicate the values of t_{CA}/t_{CR} obtained when $\theta^* = 1$, and the arrow indicates the directions of increasing $\mathcal{I}$.

3.3.6 Evolution and Lifetime in the SJ Mode

A droplet undergoing simultaneous evaporation and imbibition in the SJ mode evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \theta_{\max} - \frac{16\mathcal{E}}{\pi R_n^2} (t - t_{n-1}) - \frac{4(2\mathcal{I})^{1/2}}{R_n} (t^{1/2} - t_{n-1}^{1/2}) \quad (3.54)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and t_n and t_{SJ} are given (3.26) and (3.27), respectively. As discussed in Section 3.2.4, t_n and t_{SJ} must, in general, be evaluated numerically, which was implemented using Mathematica [238]. Figure 3.12 shows the evolutions of R and θ given by (3.54) with (3.27) for pure evaporation (dashed line), simultaneous evaporation and imbibition (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SJ} when $\theta_{\min} = 1/2$. Figure 3.13 shows $t_{\text{SJ}}/t_{\text{CR}}$ given by (3.27) for a range of values of $\mathcal{I}$ plotted as a function of $\theta_{\min}$. In particular, Figure 3.13 illustrates, similarly to the variation of t_{SS} with θ^* in the SS mode, that t_{SJ} is a monotonic function of $\theta_{\min}$, and that t_{SJ} does always lie between t_{CR} and t_{CA} . In particular, a droplet undergoing pure imbibition evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \theta_{\max} - \frac{4}{R_n} \left[2^{1/2} (t^{1/2} - t_{n-1}^{1/2}) \right] \quad (3.55)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) where t_n and t_{SJ} must, in general, be evaluated numerically, which was implemented using Mathematica [238].

3.4 Evolution and Final Depth of the Wetting Front

In this section, we determine the evolution, and hence the final depth, of the wetting front within a finitely thick, anisotropic, initially dry, porous substrate in the CR, CA, SS, and SJ modes. Following the approach outlined in Section 2.7.2 the evolution of the wetting front, $H(t)$, for simultaneous evaporation and imbibition is given by

$$H(t) = (2\mathcal{I}t)^{1/2} \quad \text{for } 0 \leq r \leq R. \quad (3.56)$$

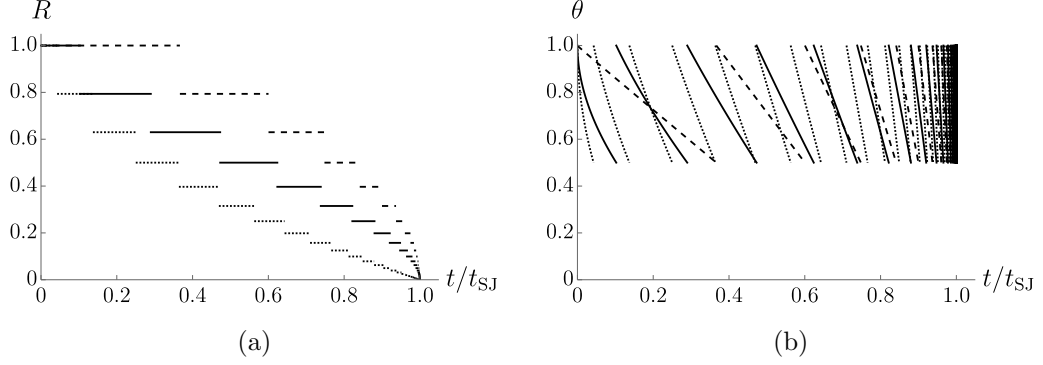


Figure 3.12: The evolutions of (a) R and (b) θ for a droplet evolving in the SJ mode given by (3.54) with (3.26) for pure evaporation (dashed line), simultaneous evaporation and imbibition (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SJ} when $\theta_{\min} = 1/2$.

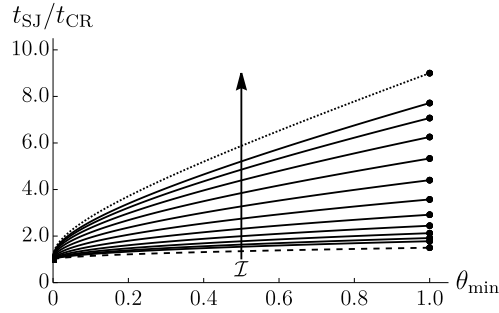


Figure 3.13: t_{SJ}/t_{CR} given by (3.27) for pure evaporation (dashed line), simultaneous evaporation $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) (solid lines), and pure imbibition (dotted line) plotted as functions of $\theta_{\min}$. The dots (•) indicate the values of t_{CA}/t_{CR} obtained in the limit $\theta_{\min} \rightarrow \theta_{\max}^- = 1^-$, and the arrow indicates the directions of increasing $\mathcal{I}$.

We determine the evolution, and hence the final depth, of the wetting front, denoted by $H_{\text{CR}} = H(t_{\text{CR}})$, $H_{\text{CA}} = H(t_{\text{CA}})$, $H_{\text{SS}} = H(t_{\text{SS}})$, and $H_{\text{SJ}} = H(t_{\text{SJ}})$ in the CR, CA, SS, and SJ modes, respectively. For a droplet undergoing pure evaporation, $H \equiv 0$ in the CR, CA, SS, and SJ modes. In contrast for pure imbibition, the wetting front evolves according to (2.56) in all four modes. Although H depends only on t (and not on r), in Figure 3.14 we plot H as a horizontal line across the r axis within the substrate. This representation emphasises that the wetting front is spatially uniform, while allowing direct visual comparison with the radial variation of the droplet height.

3.4.1 Evolution and Final Depth in the CR Mode

In the CR mode, the contact line is always pinned and, hence, the wetting front advances downwards between $0 \leq r \leq 1$. The evolution of H in terms of θ is given by solving (3.39) for t and substituting this expression into (3.56), which yields

$$H = \frac{\pi\mathcal{I}}{2^{3/2}\mathcal{E}} \left[1 + \frac{\mathcal{E}(1-\theta)}{\pi\mathcal{I}} - \left(1 + \frac{2\mathcal{E}\{1-\theta\}}{\pi\mathcal{I}} \right)^{1/2} \right]^{1/2}, \quad (3.57)$$

and so has final depth

$$H_{\text{CR}} = \frac{\pi\mathcal{I}}{2^{3/2}\mathcal{E}} \left[1 + \frac{\mathcal{E}}{\pi\mathcal{I}} - \left(1 + \frac{2\mathcal{E}}{\pi\mathcal{I}} \right)^{1/2} \right]^{1/2}. \quad (3.58)$$

Inspection of (3.57) and (3.58) reveals that, as one would expect, H and H_{CR} decrease as $\mathcal{E}$ increases. Physically H , and hence H_{CR} , decrease when the mass loss into the substrate is less than the mass loss into the atmosphere. In particular, for a droplet undergoing pure imbibition H evolves according to

$$H = \frac{1-\theta}{4}, \quad (3.59)$$

and so has final depth $H_{\text{CR}} = H_{\text{CR,I}}$ given by

$$H_{\text{CR,I}} = \frac{1}{4}. \quad (3.60)$$

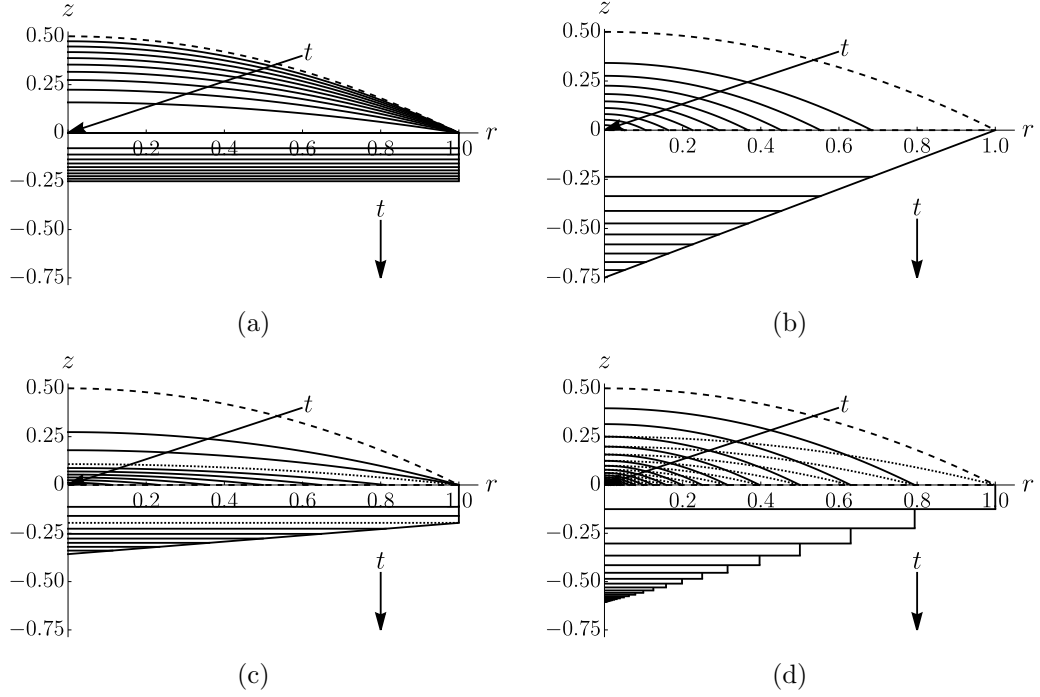


Figure 3.14: The evolutions of the free surface $z = h(r, t)$, as given by (2.8), and the wetting front $z = -H(t)$ plotted as functions of r for pure imbibition in (a) the CR mode, as given by (3.59), at $t/t_{\text{CR}} = 1/10, 1/5, \dots, 1$, (b) the CA mode, as given by (3.62), at $t/t_{\text{CA}} = 1/10, 1/5, \dots, 1$, (c) the SS mode, as given by (3.59) and (3.67) with (3.66), at $t/t_{\text{SS}} = 1/10, 1/5, \dots, 1$ when $\theta^* = 1/2$, and (d) the SJ mode, as given by (3.71) with (3.69), at $t/t_{\text{SJ}} = 1/10, 1/5, \dots, 1$ when $\theta_{\min} = 1/2$. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dotted lines in (c,d) correspond to the instant $t = t^*$ at which the contact line de-pins in the SS mode and the instants $t = t_n$ ($n = 1, 2, 3, \dots$) at which the contact line de-pins and jumps inwards to a lower value R_{n+1} , respectively. The arrows indicate the directions of increasing t .

Figure 3.14(a) shows the evolutions of the free surface $z = h(r, t)$, as given by (2.8), and the wetting front $z = -H(t)$, as given by (3.59), plotted as functions of r for pure imbibition in the CR mode at $t/t_{\text{CR}} = 1/10, 1/5, \dots, 1$. We note that the same qualitative shapes arise in the simultaneous evaporation and imbibition problem; only the depth of the wetting front differs.

3.4.2 Evolution and Final Depth in the CA Mode

In the CA mode, the contact line of the droplet and, hence, of the wetting front continually recedes. Inspection of (3.43) reveals that the evolution of t , and hence H , in the CA mode is implicit. We find that, similarly to the CR mode, H is reduced by evaporation. The final depth is obtained by substituting $t = t_{CA}$ given by (3.44) into (3.56), to yield

$$H_{CA} = \frac{1}{4} \left(\frac{3\pi\mathcal{I}}{\mathcal{E}} \right)^{1/2} \left[\frac{\pi\mathcal{I} \left(1 - \left\{ 1 - \frac{12\mathcal{E}}{\pi\mathcal{I}} \right\}^{1/2} \right)}{6\mathcal{E}} - 1 \right]^{1/2 \left(1 - \frac{12\mathcal{E}}{\pi\mathcal{I}} \right)^{-1/2}} \quad (3.61)$$

which occurs at $r = 0$. Inspection of (3.61) reveals that, similarly to the CR mode, H_{CA} is reduced by evaporation. In particular, for a droplet undergoing pure imbibition H evolves according to

$$H = \frac{3(1-R)}{4}, \quad (3.62)$$

and so has final depth $H_{CA} = H_{CA,I}$ given by

$$H_{CA,I} = \frac{3}{4}, \quad (3.63)$$

which occurs at $r = 0$. Figure 3.14(b) shows the evolutions of the free surface $z = h(r, t)$, as given by (2.8), and the wetting front $z = -H(t)$, as given by (3.62), plotted as functions of r for pure imbibition in the CA mode at $t/t_{CA} = 1/10, 1/5, \dots, 1$.

3.4.3 Evolution and Final Depth in the SS Mode

In the SS mode, H evolves according to (3.57) in the CR phase for $0 \leq t \leq t^*$, where the critical depth in the CR phase $H = H^*$ is given by

$$H^* = \frac{\pi\mathcal{I}\beta^{1/2}}{2^{3/2}\mathcal{E}}. \quad (3.64)$$

Inspection of (3.49) reveals that the evolution of t , and hence of H , in the CA phase for $t^* < t \leq t_{\text{SS}}$ is implicit. The final depth is obtained by substituting $t = t_{\text{SS}}$ given by (3.50) into (3.56), to yield

$$H_{\text{SS}} = \frac{\pi \mathcal{I}}{2^{3/2} \mathcal{E}} \left[\beta + \left(\frac{\beta}{2} \right)^{1/2} + \frac{\theta^* (1 + \mathcal{E})}{\pi \mathcal{I}} \right]^{1/2} \left[\frac{\beta + \frac{\beta^{1/2} \left(1 - \left\{ 1 - \frac{12 \mathcal{E} \theta^*}{\pi \mathcal{I}} \right\}^{1/2} \right)}{2^{3/2}}}{\beta + \frac{\beta^{1/2} \left(1 + \left\{ 1 - \frac{12 \mathcal{E} \theta^*}{\pi \mathcal{I}} \right\}^{1/2} \right)}{2^{3/2}}} \right]^{1/2} \left(1 - \frac{12 \mathcal{E} \theta^*}{\pi \mathcal{I}} \right)^{-1/2}, \quad (3.65)$$

which occurs at $r = 0$. In particular, for a droplet undergoing pure imbibition H is given by (3.59) in the CR phase for $0 \leq t \leq t^*$, where $H^* = H_{\text{I}}^*$ is given by

$$H_{\text{I}}^* = \frac{1 - \theta^*}{4} \quad (3.66)$$

and according to

$$H = \frac{3\theta^*(1 - R) + 1 - \theta^*}{4} \quad (3.67)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and so has final depth $H_{\text{SS}} = H_{\text{SS,I}}$ given by

$$H_{\text{SS,I}} = \frac{1 + 2\theta^*}{4}, \quad (3.68)$$

which occurs at $r = 0$. Figure 3.14(c) shows the evolutions of the free surface $z = h(r, t)$, as given by (2.8), and the wetting front $z = -H(t)$, as given by (3.59) and (3.67) with (3.66), plotted as functions of r for pure imbibition in the SS mode at $t/t_{\text{SS}} = 1/10, 1/5, \dots, 1$ when $\theta^* = 1/2$. Figure 3.15 shows the evolution of $H_{\text{SS}}/H_{\text{CR,I}}$ given by (3.65) as a function of θ^* for a range of $\mathcal{I}$ values. In particular, Figure 3.15 illustrates that H_{SS} is a monotonic function of θ^* , and that H_{SS} always lies between H_{CR} and H_{CA} .

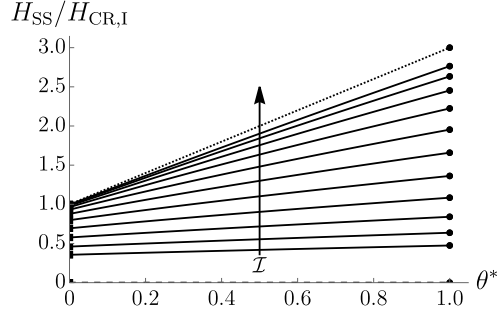


Figure 3.15: $H_{SS}/H_{CR,I}$ given by (3.65) for pure evaporation (dashed line), simultaneous evaporation $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) (solid lines), and pure imbibition (dotted line) plotted as functions of θ^* . The squares (■) indicate the values of $H_{CR}/H_{CR,I}$ obtained when $\theta^* = 0$, the dots (●) indicate the values of $H_{CA}/H_{CR,I}$ obtained when $\theta^* = 1$, and the arrow indicates the directions of increasing $\mathcal{I}$. The dotted line indicates $H_{SS,I}/H_{CR,I}$ given by (3.68) for pure imbibition and the dashed line indicates $H/H_{CR,I}$ for pure evaporation.

3.4.4 Evolution and Final Depth in the SJ Mode

In the SJ mode, the radius of the droplet, and hence of the wetting front, discontinuously recedes. The evolution of H in the n th CR phase is given by (3.56) for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and the depth at the end of the n th CR phase $H = H_n$ is given by

$$H_n = (2\mathcal{I}t_n)^{1/2} \quad (3.69)$$

in the n th CR phase for $t = t_n$ ($n = 1, 2, 3, \dots$), and so has final depth

$$H_{SJ} = (2\mathcal{I}t_{SJ})^{1/2} \quad (3.70)$$

which occurs at $r = 0$, i.e., as $n \rightarrow \infty$, and must, in general, be evaluated numerically, which we implemented using Mathematica [238]. In particular, for a droplet undergoing pure imbibition, H evolves according to

$$H = \frac{(\theta_{\max} - \theta)R_n}{4} + H_{n-1} \quad (3.71)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) and so has final depth $H_{SJ} = H_{SJ,I}$ which occurs at $r = 0$, i.e., as $n \rightarrow \infty$, and must, in general, be evaluated

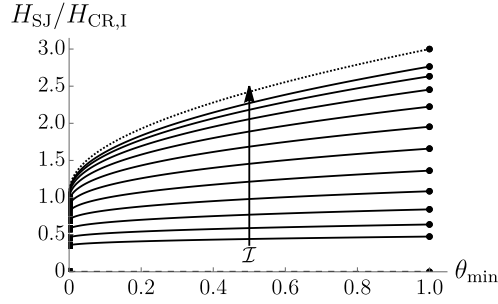


Figure 3.16: $H_{\text{SJ}}/H_{\text{CR,I}}$ given by (3.70) for pure evaporation (dashed line), simultaneous evaporation $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) (solid lines), and pure imbibition (dotted line) plotted as functions of $\theta_{\min}$. The squares (■) indicate the values of $H_{\text{CR}}/H_{\text{CR,I}}$ obtained when $\theta^* = 0$, the dots (●) indicate the values of $H_{\text{CA}}/H_{\text{CR,I}}$ obtained when $\theta^* = 1$, and the arrow indicates the directions of increasing $\mathcal{I}$. The dotted line indicates $H_{\text{SJ,I}}/H_{\text{CR,I}}$ given by (3.68) for pure imbibition and the dashed line indicates $H/H_{\text{CR,I}} = 0$ for pure evaporation.

numerically, which was implemented using Mathematica [238]. Figure 3.14(d) shows the evolutions of the free surface $z = h(r, t)$, as given by (2.8), and the wetting front $z = -H(t)$, as given by (3.71) with (3.69), plotted as functions of r for pure imbibition in the SJ mode at $t/t_{\text{SJ}} = 1/10, 1/5, \dots, 1$ when $\theta_{\min} = 1/2$. Figure 3.16 shows $H_{\text{SJ}}/H_{\text{CR,I}}$ given by (3.70) for a range of values of $\mathcal{I}$ plotted as a function of $\theta_{\min}$ when $\theta_{\max} = 1$. In particular, Figure 3.16 illustrates that, similar to H_{SS} , H_{SJ} is a monotonic function of $\theta_{\min}$, and that H_{SJ} always lies between H_{CR} and H_{CA} .

3.5 A finitely thick, anisotropic, flooded, porous substrate

In this section, we determine the evolution, and hence the lifetime, of a droplet on a finitely thick, anisotropic, flooded, porous substrate undergoing simultaneous evaporation and imbibition in the CR, CA, SS, and SJ modes. In particular, the evolution of a thin sessile droplet undergoing pure evaporation in the CR, CA, SS, and SJ modes are given in Sections 3.2.1, 3.2.2, 3.2.3, and 3.2.4, respectively.

Substituting the local evaporation mass flux J_{E} given by (2.32) and the local imbibition mass flux J_{I} given by (2.65) into the evolution equation (2.23) and performing

the integration yields

$$\frac{d(\theta R^3)}{dt} = -8R \left(\frac{2\mathcal{E}}{\pi} + \mathcal{I}\theta \right). \quad (3.72)$$

In situations in which evaporation dominates, as discussed in Section 3.2,

$$\mathcal{E} = 1 \quad \text{and} \quad \mathcal{I} = \frac{\hat{U}_{\text{I,ref}}}{\hat{U}_{\text{E,ref}}} = \frac{\hat{J}_{\text{I,ref}}}{\hat{J}_{\text{E,ref}}} = \frac{\hat{t}_{\text{E,ref}}}{\hat{t}_{\text{I,ref}}} = \frac{\hat{\rho}\hat{\theta}_0\hat{k}\hat{\gamma}}{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})}. \quad (3.73)$$

On the other hand, in situations in which imbibition dominates, as discussed in Section 3.2,

$$\mathcal{E} = \frac{\hat{U}_{\text{E,ref}}}{\hat{U}_{\text{I,ref}}} = \frac{\hat{J}_{\text{E,ref}}}{\hat{J}_{\text{I,ref}}} = \frac{\hat{t}_{\text{I,ref}}}{\hat{t}_{\text{E,ref}}} = \frac{\hat{D}(\hat{c}_{\text{sat}} - \hat{c}_{\infty})}{\hat{\rho}\hat{\theta}_0\hat{k}\hat{\gamma}} \quad \text{and} \quad \mathcal{I} = 1. \quad (3.74)$$

3.5.1 Evolution and Lifetime in the CR Mode

Setting $R \equiv 1$ in (3.72) and solving for θ shows that a droplet undergoing simultaneous evaporation and imbibition in the CR mode evolves according to

$$R \equiv 1, \quad \theta = \left(1 + \frac{2\mathcal{E}}{\pi\mathcal{I}} \right) \exp(-8\mathcal{I}t) - \frac{2\mathcal{E}}{\pi\mathcal{I}}, \quad (3.75)$$

and so has lifetime

$$t_{\text{CR}} = \frac{1}{8\mathcal{I}} \log \left(1 + \frac{\pi\mathcal{I}}{2\mathcal{E}} \right). \quad (3.76)$$

Figure 3.17(a) shows the evolution of θ given by (3.75) for a range of values of $\mathcal{I}$ plotted as a function of t/t_{CR} . In particular, (3.76) shows that, as expected, increasing the strength of evaporation and/or imbibition (i.e., increasing $\mathcal{E}$ and/or $\mathcal{I}$) shortens the lifetime of the droplet. In particular, a droplet undergoing pure imbibition evolves according to

$$R \equiv 1, \quad \theta = \exp(-8t) \rightarrow 0^+, \quad (3.77)$$

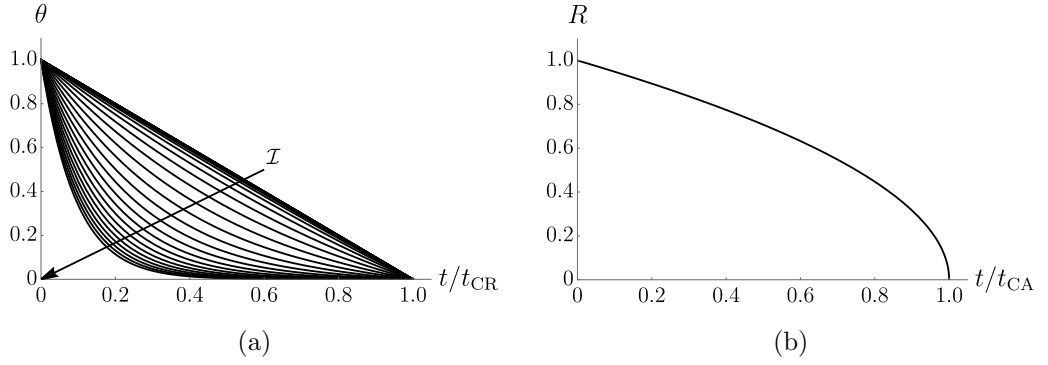


Figure 3.17: The evolutions of (a) θ for a droplet evolving in the CR mode given by (3.75) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of t/t_{CR} and (b) R for a droplet evolving in the CA mode given by (3.78) also for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of t/t_{CA} . The arrows indicate the directions of increasing $\mathcal{I}$.

and so never completely imbibes, i.e., it has an infinitely long lifetime $t_{\text{CR}} = t_{\text{CR},\text{I}} = \infty$. Similarly to the physical qualitative difference in the behaviour of a droplet undergoing pure evaporation and pure imbibition on an infinitely thick, isotropic, flooded, porous substrate in the CR mode discussed in Section 3.2.1, the physical qualitative difference in the behaviour of a droplet undergoing pure evaporation and pure imbibition in the CR mode arises because the global evaporation mass flux $F_{\text{E}} \equiv 4$ given by (2.33) remains constant as the droplet evolves because its contact line remains pinned. When combined with the droplet geometry, this leads to the finite lifetime (3.7) in the case of pure evaporation, whereas, since the leading-order pressure $p^{(0)} = 2\theta$ given by (2.9) tends to zero as the droplet evolves, the global imbibition mass flux $F_{\text{I}} \equiv 2\pi\theta$ given by (2.66) also tends to zero. When combined with the droplet geometry, this leads to an infinitely long lifetime in the case of pure imbibition.

3.5.2 Evolution and Lifetime in the CA Mode

Setting $\theta \equiv 1$ in (3.72) and solving for R shows that a droplet undergoing simultaneous evaporation and imbibition in the CA mode evolves according to

$$R = \left[1 - \frac{16}{3} \left(\mathcal{I} + \frac{2\mathcal{E}}{\pi} \right) t \right]^{1/2}, \quad \theta \equiv 1, \quad (3.78)$$

and so has lifetime

$$t_{\text{CA}} = \frac{3}{16 \left(\mathcal{I} + \frac{2\mathcal{E}}{\pi} \right)}. \quad (3.79)$$

Figure 3.17(b) shows the evolution of R given by (3.78) for a range of values of $\mathcal{I}$ plotted as a function of t/t_{CA} , and illustrates that the droplet evolves according to $R = (1 - t/t_{\text{CA}})^{1/2}$ regardless of the relative strength of $\mathcal{E}$ and/or $\mathcal{I}$. In particular, (3.79) shows that, as in the CR mode, increasing $\mathcal{E}$ and/or $\mathcal{I}$ shortens the lifetime of the droplet. In particular, a droplet undergoing pure imbibition evolves according to

$$R = \left(1 - \frac{16}{3}t \right)^{1/2}, \quad \theta \equiv 1, \quad (3.80)$$

and so has lifetime $t_{\text{CA}} = t_{\text{CA,I}}$ given by

$$t_{\text{CA,I}} = \frac{3}{16}. \quad (3.81)$$

According to (3.80) R^2 and $V^{2/3}$ are both linear in t , and so by analogy we could term these results as the “ d^2 law” and the “ $2/3$ law” of pure imbibition, respectively. Physically, the qualitative difference in the behaviour of a droplet undergoing pure imbibition in the CR and CA modes arises because the global imbibition mass flux, given by (2.66), tends to zero in the CR mode, $F_{\text{I}} \equiv 2\pi\theta$, as the droplet imbibes. When combined with the droplet geometry, this leads to an infinitely long lifetime. In the CA mode, by contrast, the leading-order pressure within the droplet, $p^{(0)} = 2/R$ given by (2.9), tends to infinity as the droplet imbibes and $F_{\text{I}} \equiv 2\pi R$ tends to zero. When combined with the droplet geometry, this leads to the finite lifetime (3.81).

3.5.3 Evolution and Lifetime in the SS Mode

A droplet undergoing simultaneous evaporation and imbibition in the SS mode evolves according to (3.75) in the CR phase for $0 \leq t \leq t^*$, where

$$t^* = \frac{1}{8\mathcal{I}} \log \left(\frac{1 + \frac{2\mathcal{E}}{\pi\mathcal{I}}}{\theta^* + \frac{2\mathcal{E}}{\pi\mathcal{I}}} \right), \quad (3.82)$$

and according to

$$R = \left[1 - \frac{16}{3} \left(\mathcal{I} + \frac{2\mathcal{E}}{\pi\theta^*} \right) \{t - t^*\} \right]^{1/2}, \quad \theta \equiv \theta^* \quad (3.83)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and so has lifetime

$$t_{\text{SS}} = \frac{1}{8\mathcal{I}} \left[\frac{3\theta^*}{2 \left(\theta^* + \frac{2\mathcal{E}}{\pi\mathcal{I}} \right)} + \log \left(\frac{1 + \frac{2\mathcal{E}}{\pi\mathcal{I}}}{\theta^* + \frac{2\mathcal{E}}{\pi\mathcal{I}}} \right) \right]. \quad (3.84)$$

Figure 3.18 shows the evolutions of R and θ given by (3.83) and (3.75) with (3.82) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SS} when $\theta^* = 1/2$. Figure 3.19 shows $t_{\text{SS}}/t_{\text{CR}}$ given by (3.17) for a range of values of $\mathcal{I}$ plotted as a function of θ^* . In particular, Figure 3.19 illustrates that t_{SS} is, in general, a non-monotonic function of θ^* , and that t_{SS} does not, as might have naively been expected, always lie between t_{CR} and t_{CA} . In particular, a droplet undergoing pure imbibition evolves according to (3.77) in the CR phase for $0 \leq t \leq t^*$, where $t^* = t_1^*$ is given by

$$t_1^* = \frac{1}{8} (-\log \theta^*), \quad (3.85)$$

and according to

$$R = \left[1 - \frac{16}{3} (t - t_1^*) \right]^{1/2}, \quad \theta \equiv \theta^* \quad (3.86)$$

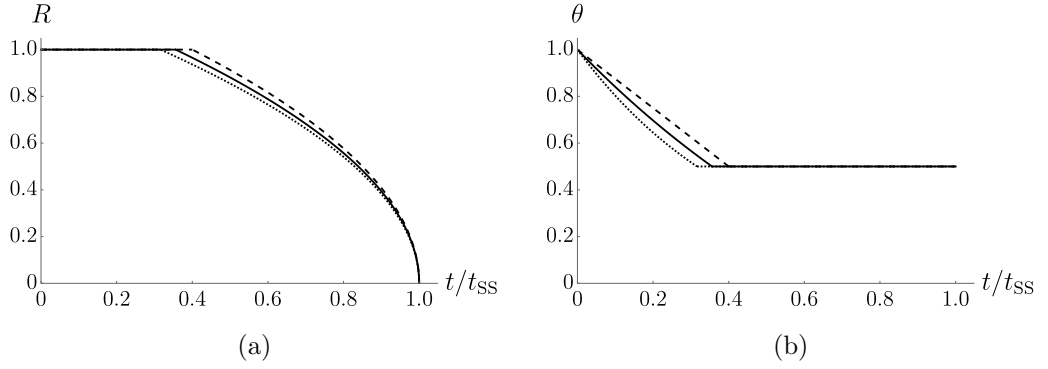


Figure 3.18: The evolutions of (a) R and (b) θ for a droplet evolving in the SS mode given by (3.83) and (3.75) with (3.82) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SS} when $\theta^* = 1/2$.

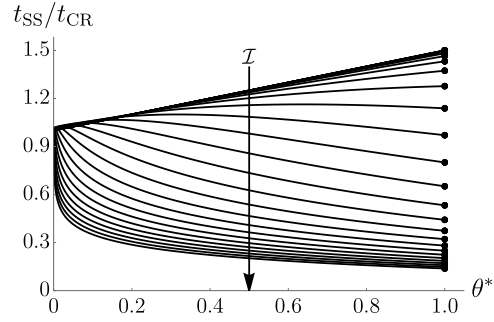


Figure 3.19: t_{SS}/t_{CR} given by (3.84) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of θ^* . The dots ($\bullet$) indicate the values of t_{CA}/t_{CR} obtained when $\theta^* = 1$, and the arrow indicates the directions of increasing $\mathcal{I}$.

in the CA phase for $t^* < t \leq t_{SS}$, and so has lifetime $t_{SS} = t_{SS,I}$ given by

$$t_{SS,I} = \frac{1}{16} (3 - 2 \log \theta^*). \quad (3.87)$$

3.5.4 Evolution and Lifetime in the SJ Mode

A droplet undergoing simultaneous evaporation and imbibition in the SJ mode evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \left(\theta_{\max} + \frac{2\mathcal{E}}{\pi\mathcal{I}} \right) \exp \left[-\frac{8\mathcal{I}}{R_n^2} (t - t_{n-1}) \right] - \frac{2\mathcal{E}}{\pi\mathcal{I}} \quad (3.88)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), the duration of the n th CR phase, denoted by $\delta t_n = t_n - t_{n-1}$, is given by

$$\delta t_n = \frac{1}{8\mathcal{I}} \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2(n-1)/3} \log \left[\frac{\theta_{\max} + \frac{2\mathcal{E}}{\pi\mathcal{I}}}{\theta_{\min} + \frac{2\mathcal{E}}{\pi\mathcal{I}}} \right], \quad (3.89)$$

and t_n and t_{SJ} are given (3.26) and (3.27), respectively. As discussed in Section 3.2.4, t_n and t_{SJ} must, in general, be evaluated numerically, which was implemented using Mathematica [238]. Figure 3.20 shows the evolutions of R and θ given by (3.88) with (3.26) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SJ} when $\theta_{\min} = 1/2$. Figure 3.21 shows $t_{\text{SJ}}/t_{\text{CR}}$ given by (3.27) for a range of values of $\mathcal{I}$ plotted as a function of $\theta_{\min}$. In particular, Figure 3.21 illustrates, similarly to the variation of t_{SS} with θ^* in the SS mode, that t_{SJ} is, in general, a non-monotonic function of $\theta_{\min}$, and that t_{SJ} does not, as might have naively been expected, always lie between t_{CR} and t_{CA} . In particular, a droplet undergoing pure imbibition evolves according to

$$R \equiv R_n = \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{(n-1)/3}, \quad \theta = \theta_{\max} \exp \left[-\frac{8}{R_n^2} (t - t_{n-1}) \right] \quad (3.90)$$

in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), with

$$\delta t_{n,\text{I}} = \frac{1}{8} \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2(n-1)/3} \log \left(\frac{\theta_{\max}}{\theta_{\min}} \right) \quad (3.91)$$

and

$$t_{n,\text{I}} = \frac{1}{8} \left[\frac{1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2n/3}}{1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2/3}} \right] \log \left(\frac{\theta_{\max}}{\theta_{\min}} \right), \quad (3.92)$$

and so has lifetime $t_{\text{SJ}} = t_{\text{SJ,I}}$ given by

$$t_{\text{SJ,I}} = \frac{\theta_{\max}^{2/3}}{8 \left(\theta_{\max}^{2/3} - \theta_{\min}^{2/3} \right)} \log \left(\frac{\theta_{\max}}{\theta_{\min}} \right). \quad (3.93)$$

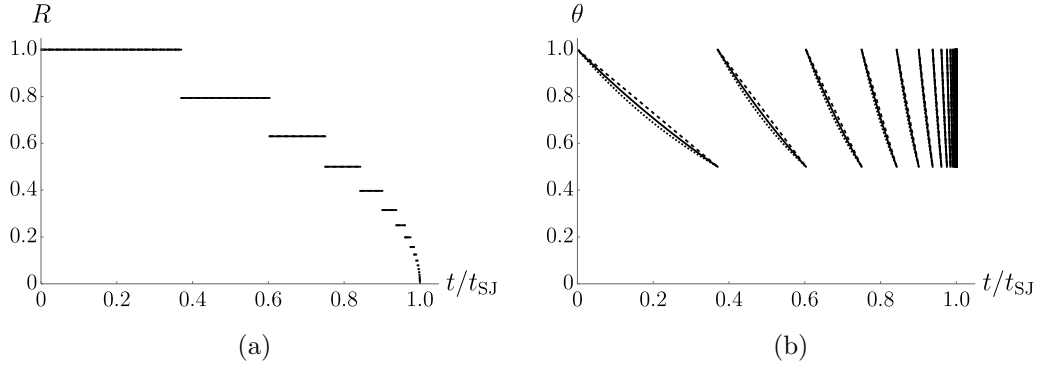


Figure 3.20: The evolutions of (a) R and (b) θ for a droplet evolving in the SJ mode given by (3.88) with (3.26) for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) plotted as functions of t/t_{SJ} when $\theta_{\min} = 1/2$.

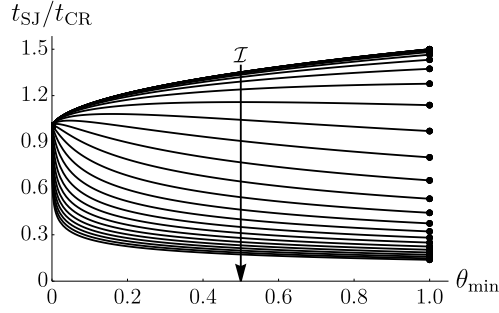


Figure 3.21: $t_{\text{SJ}}/t_{\text{CR}}$ given by (3.27) for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) plotted as a function of $\theta_{\min}$. The dots ($\bullet$) indicate the values of $t_{\text{CA}}/t_{\text{CR}}$ obtained in the limit $\theta_{\min} \rightarrow \theta_{\max}^- = 1^-$, and the arrow indicates the directions of increasing $\mathcal{I}$.

3.6 Conclusions

In Chapter 3 we have analysed mathematical models for the evolution, and hence the lifetime, of a thin sessile droplet undergoing simultaneous evaporation and imbibition in the CR, CA, SS, and SJ modes. In particular, analytical expressions for the evolution of the droplet are obtained for droplets evolving in four different modes, on three different porous substrates.

In Section 3.2 we determined the evolution, and hence the lifetime, of a thin sessile droplet on an infinitely thick, isotropic, flooded, porous substrate in the CR, CA, SS, and SJ modes. A droplet undergoing pure evaporation in the CR mode has a finite lifetime, whereas a droplet undergoing pure imbibition in the CR mode never completely

imbibes, i.e., it has an infinitely long lifetime. In the CA mode, the reduction in the global evaporation mass flux leads to an extended lifetime (when compared with the CR mode) in the case of pure evaporation, while a droplet undergoing pure imbibition in the CA mode has a finite lifetime. In the SS and SJ modes the lifetime is, in general, a non-monotonic function of θ^* and $\theta_{\min}$, respectively, and does not always lie between t_{CR} and t_{CA} .

In Sections 3.3 and 3.4 we determined the evolution, and hence the lifetime, of a thin sessile droplet on a finitely thick, anisotropic, initially dry, porous substrate, together with the evolution, and hence the final depth, of the wetting front, in the CR, CA, SS, and SJ modes. In contrast to Section 3.2, where a droplet undergoing pure imbibition in the CR mode never completely imbibes and hence has an infinitely long lifetime, a droplet undergoing pure imbibition in the CR mode has a finite lifetime. Comparison with the experimental results of the investigations of Li *et al.* [6], Willis *et al.* [10], and Richards *et al.* [11] in the CR mode showed good quantitative agreement with the model for the evolution of a droplet in the CR mode. Under the experimental conditions of Li *et al.* [6], which correspond to a relatively small $\mathcal{E}$, the predicted droplet lifetime for simultaneous evaporation and imbibition was approximately 1–4% shorter than that for pure imbibition. Under the experimental conditions of Willis *et al.* [10] and Richards *et al.* [11], which correspond to a relatively small $\mathcal{I}$, the predicted droplet lifetime for simultaneous evaporation and imbibition was 39–56% and approximately 13% shorter than that for pure evaporation, respectively. Furthermore, while in Section 3.2 the SS and SJ mode lifetimes are, in general, non-monotonic functions of θ^* and $\theta_{\min}$, respectively, in Section 3.3 the SS and SJ mode lifetimes are monotonic functions of θ^* and $\theta_{\min}$, respectively, and so always lie between t_{CR} and t_{CA} . Analysis of the evolution of the wetting front showed that the final depth is reduced as the evaporation number increases (or the imbibition number decreases), and that in the SS and SJ modes the final depths are monotonic functions of θ^* and $\theta_{\min}$, respectively, and so always lie between H_{CR} and H_{CA} . In particular, the shape of the final volume of the wetting front within the substrate are a cylinder, cone, a combination of both, and a tiered cylinder in the CR, CA, SS, and SJ modes, respectively.

In Section 3.5 we determined the evolution, and hence the lifetime, of a thin sessile droplet on a finitely thick, anisotropic, flooded, porous substrate in the CR, CA, SS, and SJ modes. Similarly to Section 3.2, a droplet undergoing pure imbibition in the CR mode never completely imbibes and the SS and SJ mode lifetimes are, in general, non-monotonic functions of θ^* and $\theta_{\min}$, respectively. In contrast, the governing laws for the evolution of R in the CA mode differ between Sections 3.2 and 3.5, in Section 3.2 the evolution of R follows the “ d^3 law”, whereas in Section 3.5, in the same manner as pure evaporation, it follows the “ d^2 law”. We note that it would be interesting to experimentally investigate the critical substrate thickness where the transition from the “ d^3 law” to the “ d^2 law” occurs on a flooded isotropic porous substrate, as the imbibition problem formulated in Section 2.7.3 also describes a thin, isotropic, flooded, porous substrate, as discussed in Section 2.7.3.

As shown in Sections 3.3.2 and 3.3.3, the experimental results compared with the mathematical model for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, initially dry, porous substrate in the CR mode, developed in Section 3.3, show good quantitative agreement. However, the lack of available data within the literature for the evolution of a droplet undergoing simultaneous evaporation and imbibition prevents further assessment of the mathematical models developed within Chapter 4. While the evolutionary dynamics of the pure evaporation problem are firmly established within the current literature, those of imbibition are not, and further experimental investigation is required to verify and validate these mathematical models, which provide a clear and comprehensive starting point for future experimental investigations. Having determined the evolution, and hence the lifetime, of a thin sessile droplet, in Chapter 4 we consider the implications that the evolutionary dynamics have on the flow within the droplet and the substrate.

Chapter 4

Flow Within the Droplet and the Substrate

4.1 Overview

In this chapter, we determine the flow within the droplet and the substrate in the CR, CA, SS, and SJ modes. In Section 4.2, we determine the flow within the droplet and the substrate on an infinitely thick, isotropic, flooded, porous substrate, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.1, respectively. In Section 4.3, we determine general solutions for the flow within the droplet and the substrate, where the evaporation problem is described in Section 2.6 and the imbibition problem is described by a local imbibition mass flux that is spatially uniform. The general solutions for the flow within the droplet and the substrate encompass (but are not exclusive to) the imbibition problems described in Sections 2.7.2 and 2.7.3, respectively. Also in Section 4.3, after determining general solutions for the flow within the droplet and substrate, we then determine the flow within the droplet and the substrate for a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry or flooded, porous substrate, as described in Sections 2.7.2 and 2.7.3, respectively.

4.2 An infinitely thick, isotropic, flooded, porous substrate

4.2.1 Flow in the CR Mode

Substituting the expressions for h , J_E , J_I , R , and θ given by (2.8), (2.32), (2.44), and (3.4) respectively, into (2.20), and evaluating the integral, the local radial volume flux Q is given by

$$Q = \frac{2(\mathcal{E} + 2\mathcal{I}\theta)}{\pi r} \left[(1 - r^2)^{1/2} - (1 - r^2)^2 \right], \quad (4.1)$$

and hence from (2.19) the depth-averaged velocity $\bar{u}$ is given by

$$\bar{u} = \frac{4(\mathcal{E} + 2\mathcal{I}\theta)}{\pi \theta r} \left[(1 - r^2)^{-1/2} - (1 - r^2) \right]. \quad (4.2)$$

Evaluating (2.21) using (4.1) the radial and axial components of the velocity within the droplet u and w are given by

$$u = \frac{24(\mathcal{E} + 2\mathcal{I}\theta)z}{\pi \theta^3 r (1 - r^2)^{5/2}} \left[1 - (1 - r^2)^{3/2} \right] \left[\theta (1 - r^2) - z \right] \quad (4.3)$$

and

$$w = \frac{4(\mathcal{E} + 2\mathcal{I}\theta)z^2}{\pi \theta^3 (1 - r^2)^{7/2}} \left[\left\{ 10 - 4(1 - r^2)^{3/2} \right\} z - 9\theta (1 - r^2) \right] - \frac{4\mathcal{I}\theta}{\pi (1 - r^2)^{1/2}}, \quad (4.4)$$

while evaluating (2.37) using (2.43) the radial and axial components of the velocity within the substrate U and W are given by

$$U = \frac{8\mathcal{I}\theta \left(\frac{1+r}{[(1+r)^2 + z^2]^{1/2}} - \frac{1-r}{[(1-r)^2 + z^2]^{1/2}} \right)}{\pi \varphi d_{\text{CR}} (d_{\text{CR}}^2 - 4)^{1/2}} \quad (4.5)$$

and

$$W = \frac{8\mathcal{I}\theta z^s \left(\frac{1}{[(1+r)^2 + z^s]^ {1/2}} - \frac{1}{[(1-r)^2 + z^s]^ {1/2}} \right)}{\pi\varphi d_{\text{CR}} (d_{\text{CR}}^2 - 4)^{1/2}}, \quad (4.6)$$

where we have introduced the notation

$$d_{\text{CR}} = [(1+r)^2 + z^s]^ {1/2} + [(1-r)^2 + z^s]^ {1/2}. \quad (4.7)$$

For a droplet undergoing pure evaporation, equations (4.1), (4.2), (4.3), and (4.4) reduce to the corresponding expressions as given by several previous authors (see, for example, Boulogne *et al.* [79], Gelderblom *et al.* [16], and Wilson & D'Ambrosio [17]). Note that Gelderblom *et al.* [16] define $Q = h\bar{u}r$, and so their expression for Q is equivalent to Qr in the present work. For a droplet undergoing pure evaporation Q is given by

$$Q = \frac{2}{\pi r} \left[(1-r^2)^{1/2} - (1-r^2)^2 \right], \quad (4.8)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{4}{\pi\theta r} \left[(1-r^2)^{-1/2} - (1-r^2) \right]. \quad (4.9)$$

Evaluating (2.21) using (4.8) u and w are given by

$$u = \frac{24z}{\pi\theta^3 r (1-r^2)^{5/2}} \left[1 - (1-r^2)^{3/2} \right] \left[\theta (1-r^2) - z \right] \quad (4.10)$$

and

$$w = \frac{4z^2}{\pi\theta^3 (1-r^2)^{7/2}} \left[\left\{ 10 - 4(1-r^2)^{3/2} \right\} z - 9\theta (1-r^2) \right], \quad (4.11)$$

while $U = W \equiv 0$. For a droplet undergoing pure imbibition Q is given by

$$Q = \frac{4\theta}{\pi r} \left[(1-r^2)^{1/2} - (1-r^2)^2 \right], \quad (4.12)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{8}{\pi r} \left[(1 - r^2)^{-1/2} - (1 - r^2) \right]. \quad (4.13)$$

Evaluating (2.21) using (4.13) u and w are given by

$$u = \frac{48z}{\pi\theta^2 r (1 - r^2)^{5/2}} \left[1 - (1 - r^2)^{3/2} \right] \left[\theta (1 - r^2) - z \right] \quad (4.14)$$

and

$$w = \frac{8z^2}{\pi\theta^2 (1 - r^2)^{7/2}} \left[\left\{ 10 - 4(1 - r^2)^{3/2} \right\} z - 9\theta (1 - r^2) \right] - \frac{4\theta}{\pi (1 - r^2)^{1/2}}, \quad (4.15)$$

while U and W are given by (4.5) and (4.6), respectively, with $\mathcal{I} = 1$.

We note that Q , $\bar{u}$, u and $w + \mathcal{I}J_I$ depend on $\mathcal{E}$ and $\mathcal{I}$ in the combination of $\mathcal{E} + 2\mathcal{I}\theta$, while U and W depend linearly on $\mathcal{I}\theta$ but are independent of $\mathcal{E}$. Inspection of (4.1), (4.2), (4.3), and (4.4) reveals that $Q \geq 0$, $\bar{u} \geq 0$, $u \geq 0$, and $w \leq 0$, i.e., the flow is always outwards and downwards in both the droplet and the substrate. In particular, $Q = O(r) \rightarrow 0^+$ and $\bar{u} = O(r) \rightarrow 0^+$ as $r \rightarrow 0^+$ and $Q = O((1 - r)^{1/2}) \rightarrow 0^+$ and $\bar{u} = O((1 - r)^{-1/2}) \rightarrow \infty$ as $r \rightarrow 1^-$. We note that due to the functional similarities of J_E and J_I (i.e., both being $\propto (1 - r^2)^{-1/2}$) the behaviour of Q and $\bar{u}$ at the centre and contact line of the droplet for the pure evaporation and imbibition problems are consistent with the simultaneous evaporation and imbibition problem.

Figure 4.1 shows instantaneous streamlines of the flow within a droplet evolving in the CR mode calculated from equations (4.3), (4.4), (4.5), and (4.6) for (a) pure evaporation and (b) simultaneous evaporation and imbibition (solid lines) and pure imbibition (dotted lines), all for the same value of θ . Note that, because they are for the same value of θ , the flow within the substrate is identical for the two situations shown in Figure 4.1(b). Figure 4.2 shows the evolutions of Q as functions of r for a range of values of θ for (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure imbibition. In particular, Figure 4.2(a) illustrates that Q does not change (i.e., is independent of t) as the droplet evolves for a droplet undergoing pure evaporation

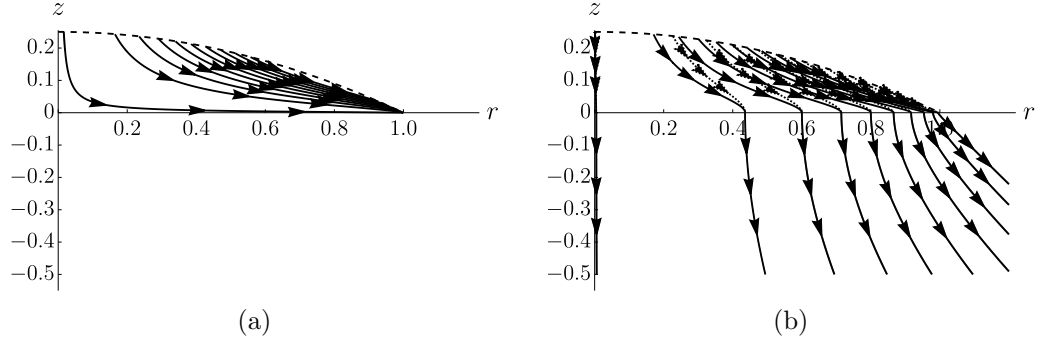


Figure 4.1: Instantaneous streamlines of the flow within the droplet and the substrate for a droplet evolving in the CR mode calculated from (4.3), (4.4), (4.5), and (4.6) for (a) pure evaporation and (b) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid lines) and pure imbibition (dotted lines), when $\theta = 1/2$.

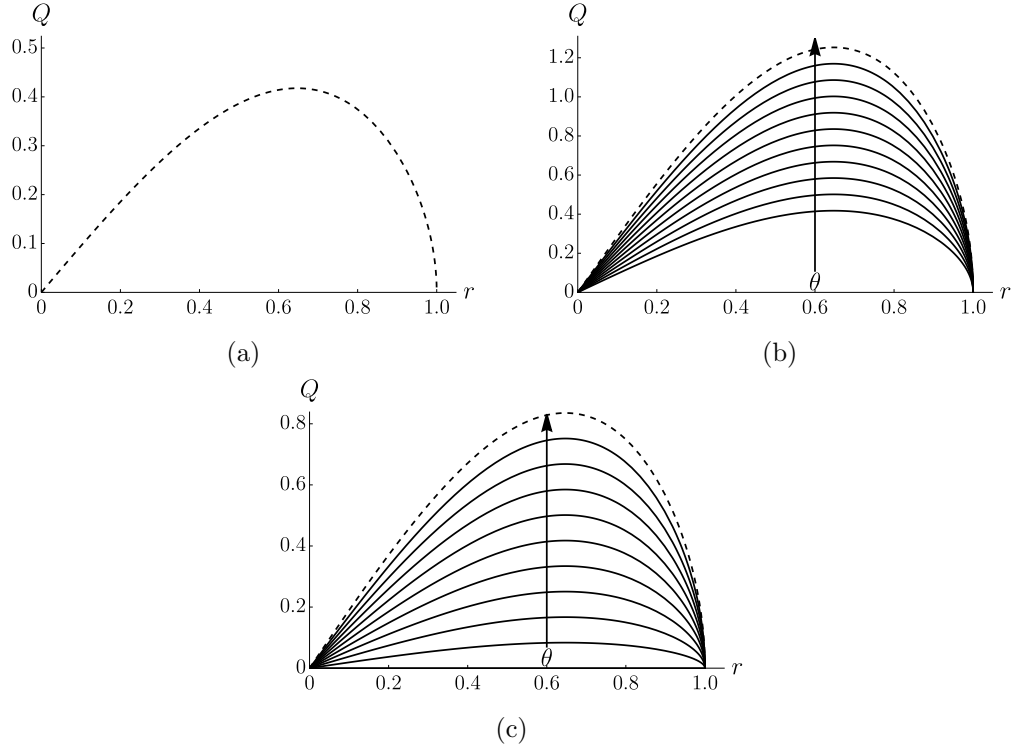


Figure 4.2: Q given by (4.1) in the CR mode plotted as functions of r for $\theta = 1/10, 2/5, \dots, 9/10$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed lines indicate the initial profile of Q at $\theta = 1$ (i.e., at $t = 0$) and the arrows indicate the directions of increasing θ .

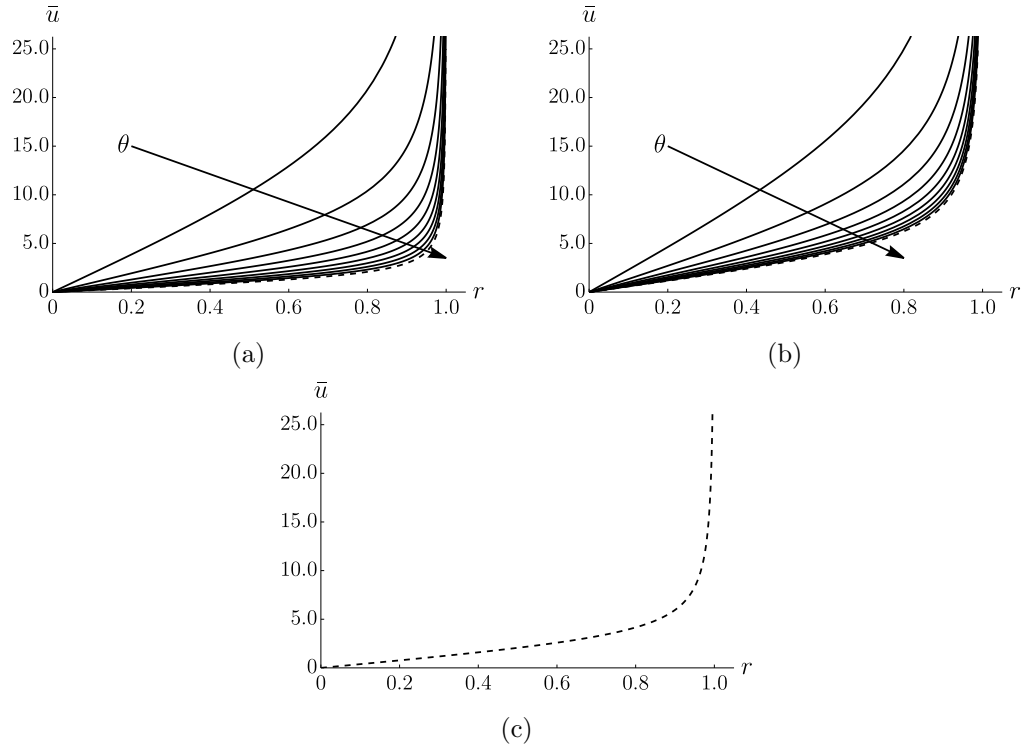


Figure 4.3: $\bar{u}$ given by (4.2) in the CR mode plotted as functions of r for $\theta = 1/10, 2/5, \dots, 9/10$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed lines indicate the initial profile of $\bar{u}$ at $\theta = 1$ (i.e., at $t = 0$) and the arrows indicate the directions of increasing θ .

and takes its maximum value of $Q \simeq 0.4177$ at $r/R \simeq 0.6470$. In contrast, Figures 4.2(b,c) illustrate that Q decreases as the droplet evolves for a droplet undergoing simultaneous evaporation and imbibition and pure imbibition, respectively. Figure 4.3 shows the evolutions of $\bar{u}$ as functions of r for a range of values of θ for (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure imbibition. In particular, Figures 4.3(a,b) illustrate that $\bar{u}$ increases as the droplet evolves for a droplet undergoing pure evaporation and simultaneous evaporation and imbibition. In contrast, Figure 4.3(c) illustrates that $\bar{u}$ does not change (i.e., is independent of t) as the droplet evolves for a droplet undergoing pure imbibition. Furthermore, Figures 4.2(b) and 4.3(b) illustrate that towards the end of the lifetime of the droplet (i.e., as $t \rightarrow t_{\text{CR}}^-$) the evaporation contribution dominates the mean flow within the droplet.

4.2.2 Flow in the CA Mode

Substituting the expressions for h , J_E , J_I , R , and θ given by (2.8), (2.32), (2.44), and (3.9) respectively, into (2.20), and evaluating the integral, Q is given by

$$Q = \frac{2(\mathcal{E}R + 2\mathcal{I})}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{1/2} - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right) \right], \quad (4.16)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{4(\mathcal{E}R + 2\mathcal{I})}{\pi Rr} \left[\left(1 - \frac{r^2}{R^2}\right)^{-1/2} - \left(1 + \frac{r^2}{3R^2}\right) \right]. \quad (4.17)$$

Evaluating (2.21) using (4.16) u and w are given by

$$u = \frac{24(\mathcal{E}R + 2\mathcal{I})z}{\pi R^3 r \left(1 - \frac{r^2}{R^2}\right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right] \left[R \left(1 - \frac{r^2}{R^2}\right) - z \right] \quad (4.18)$$

and

$$w = \frac{8(\mathcal{E}R + 2\mathcal{I})z^2}{\pi R^5 \left(1 - \frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\ \left. + R \left(1 - \frac{r^2}{R^2}\right) \left(-\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2}\right) \right] - \frac{4\mathcal{I}}{\pi R^2 \left(1 - \frac{r^2}{R^2}\right)^{1/2}}, \quad (4.19)$$

while evaluating (2.37) using (2.43) U and W are given by

$$U = \frac{8\mathcal{I} \left(\frac{R+r}{[(R+r)^2 + z^2]^{1/2}} - \frac{R-r}{[(R-r)^2 + z^2]^{1/2}} \right)}{\pi \varphi d_{\text{CA}} (d_{\text{CA}}^2 - 4R^2)^{1/2}} \quad (4.20)$$

and

$$W = \frac{8\mathcal{I}z^s \left(\frac{1}{[(R+r)^2 + z^2]^{1/2}} - \frac{1}{[(R-r)^2 + z^2]^{1/2}} \right)}{\pi \varphi d_{\text{CA}} (d_{\text{CA}}^2 - 4R^2)^{1/2}}, \quad (4.21)$$

where we have introduced the notation

$$d_{\text{CA}} = [(R+r)^2 + z^2]^{1/2} + [(R-r)^2 + z^2]^{1/2}. \quad (4.22)$$

For a droplet undergoing pure evaporation Q is given by

$$Q = \frac{2R}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{1/2} - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right) \right], \quad (4.23)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{4}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{-1/2} - \left(1 + \frac{r^2}{3R^2}\right) \right]. \quad (4.24)$$

Evaluating (2.21) using (4.23) u and w are given by

$$u = \frac{24z}{\pi R^2 r \left(1 - \frac{r^2}{R^2}\right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right] \left[R \left(1 - \frac{r^2}{R^2}\right) - z \right] \quad (4.25)$$

and

$$w = \frac{8Rz^2}{\pi R^5 \left(1 - \frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\ \left. + R \left(1 - \frac{r^2}{R^2}\right) \left\{ -\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right\} \right], \quad (4.26)$$

while $U = W \equiv 0$ (see Gelderblom *et al.* [16] and D'Ambrosio *et al.* [84]). For a droplet undergoing pure imbibition Q is given by

$$Q = \frac{4}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{1/2} - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right) \right], \quad (4.27)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{8}{\pi R r} \left[\left(1 - \frac{r^2}{R^2}\right)^{-1/2} - \left(1 + \frac{r^2}{3R^2}\right) \right]. \quad (4.28)$$

Evaluating (2.21) using (4.27) u and w are given by

$$u = \frac{48z}{\pi R^3 r \left(1 - \frac{r^2}{R^2}\right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right] \left[R \left(1 - \frac{r^2}{R^2}\right) - z \right] \quad (4.29)$$

and

$$w = \frac{16z^2}{\pi R^5 \left(1 - \frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\ \left. + R \left(1 - \frac{r^2}{R^2}\right) \left\{ -\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right\} \right] - \frac{4}{\pi R^2 \left(1 - \frac{r^2}{R^2}\right)^{1/2}}, \quad (4.30)$$

while U and W are given by (4.20) and (4.21), respectively, with $\mathcal{I} = 1$.

We note that Q , $\bar{u}$, u and $w + \mathcal{I}J_1$ depend on $\mathcal{E}$ and $\mathcal{I}$ in the combination $\mathcal{E}R + 2\mathcal{I}$, while U and W depend linearly on $\mathcal{I}$ but are independent of $\mathcal{E}$. Inspection of (4.16), (4.17), (4.18), and (4.19) reveals that $Q \geq 0$, $\bar{u} \geq 0$, $u \geq 0$, and $w \leq 0$, i.e., the flow is always outwards and downwards in both the droplet and the substrate. In particular,

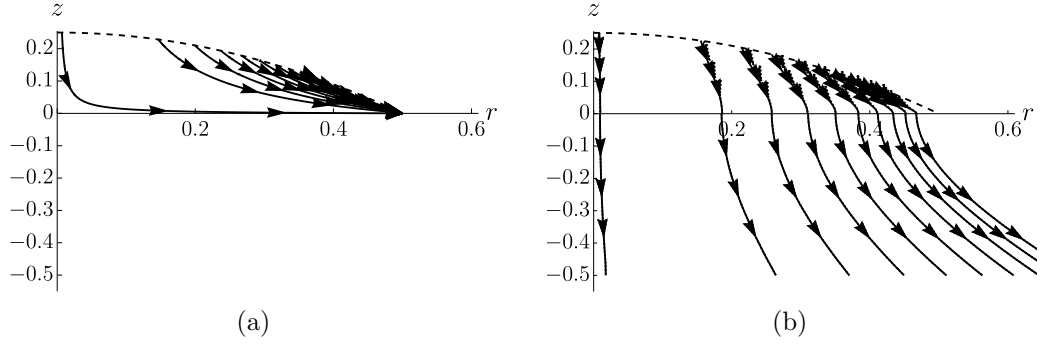


Figure 4.4: Instantaneous streamlines of the flow within the droplet and the substrate for a droplet evolving in the CA mode calculated from (4.18), (4.19), (4.20), and (4.21) for (a) pure evaporation and (b) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid lines) and pure imbibition (dotted lines), when $R = 1/2$.

$Q = O(r) \rightarrow 0^+$ and $\bar{u} = O(r) \rightarrow 0^+$ as $r \rightarrow 0^+$ and $Q = O((R - r)^{1/2}) \rightarrow 0^+$ and $\bar{u} = O((R - r)^{-1/2}) \rightarrow \infty$ as $r \rightarrow R^-$. We note that due to the functional similarities of J_E and J_I (i.e. both being $\propto (R^2 - r^2)^{-1/2}$) the behaviour of Q and $\bar{u}$ at the centre and contact line of the droplet for the pure evaporation and imbibition problems are consistent with the simultaneous evaporation and imbibition problem.

Figure 4.4 shows instantaneous streamlines of the flow for a droplet evolving in the CA mode calculated from equations (4.18), (4.19), (4.20), and (4.21) for (a) pure evaporation and (b) simultaneous evaporation and imbibition (solid lines) and pure imbibition (dotted lines), all for the same value of R . Note that, because they are for the same value of R , the flow within the substrate is identical for the two situations shown in Figure 4.4(b). Figure 4.5 shows the evolutions of Q as functions of r for a range of values of R for (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure imbibition. In particular, Figure 4.5(a) illustrates that Q is self-similar and also that the behaviour is identical as the droplet evolves when scaled with r/R , and takes its maximum value of $Q \simeq 0.1383$ at $r/R \simeq 0.8824$. In contrast, Figures 4.5(b,c) illustrate that Q increases as the droplet evolves for a droplet undergoing pure imbibition or simultaneous evaporation and imbibition. Figure 4.6 shows the evolutions of $\bar{u}$ as functions of r for a range of values of R for (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure imbibition. In particular, Figure

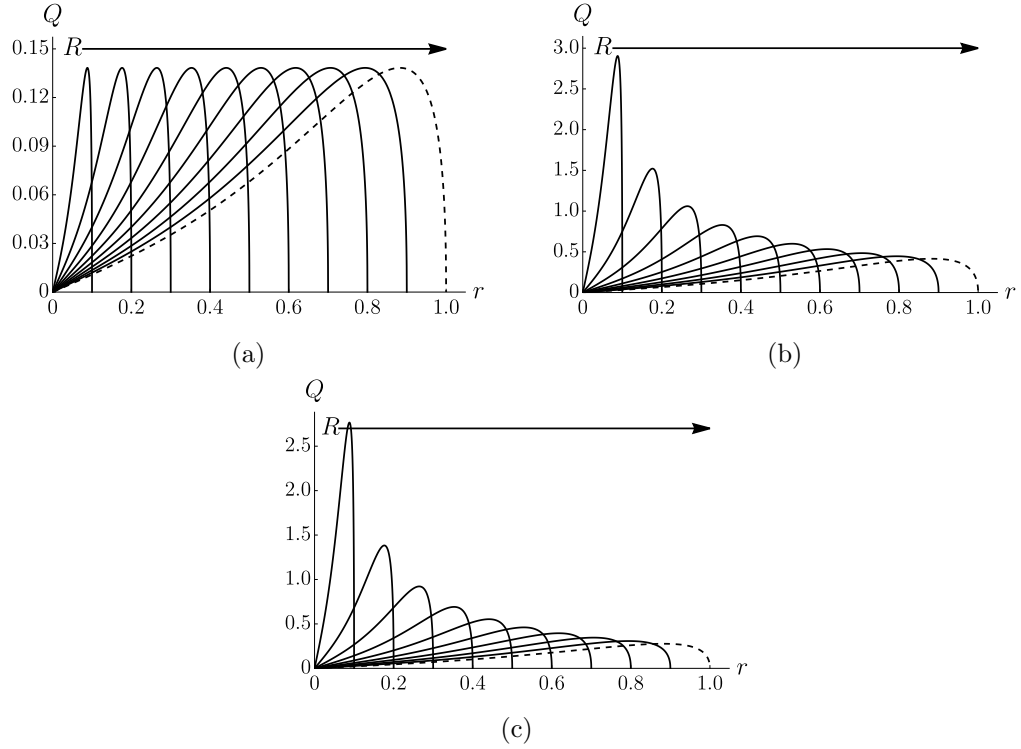


Figure 4.5: Q given by (4.16) in the CA mode plotted as functions of r for $R = 1/10, 2/5, \dots, 9/10$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed lines indicate the initial profile of Q at $R = 1$ (i.e., at $t = 0$) and the arrows indicate the directions of increasing R .

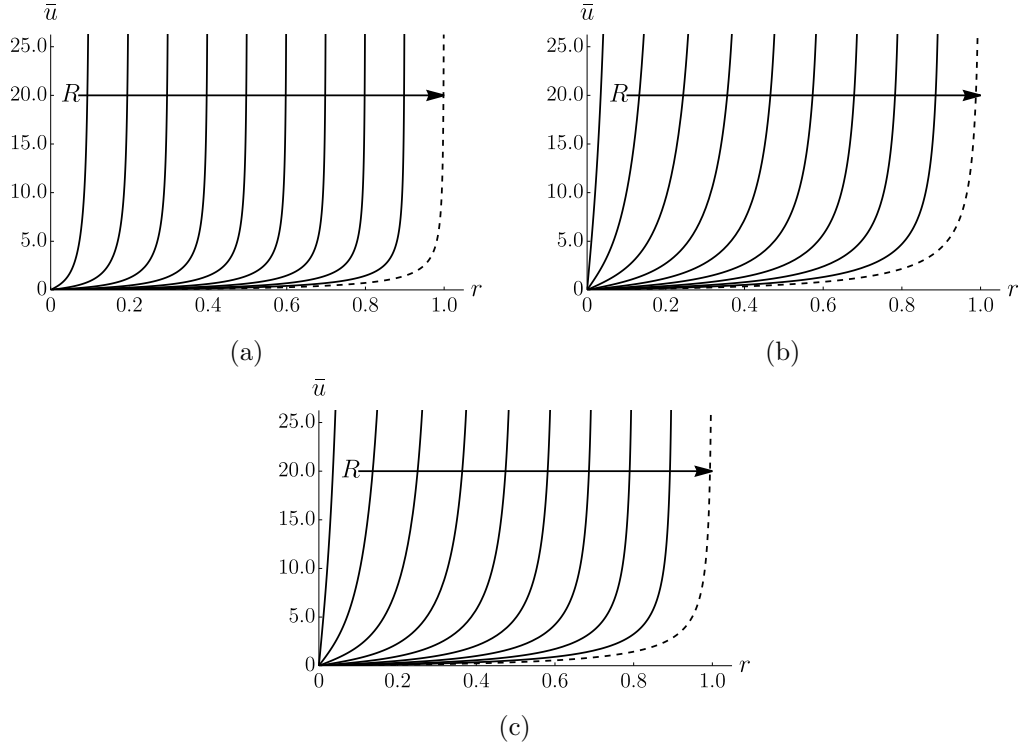


Figure 4.6: $\bar{u}$ given by (4.17) in the CA mode plotted as functions of r for $R = 1/10, 2/5, \dots, 9/10$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed lines indicate the initial profile of $\bar{u}$ at $R = 1$ (i.e., at $t = 0$) and the arrows indicate the directions of increasing R .

4.6 illustrates that $\bar{u}$ increases as the droplet evolves. In summary, although the CR and CA modes differ in whether the contact line moves, the flow in both cases remains directed outwards towards the contact line, so the two flow profiles are qualitatively similar apart from the distinct contact-line motion.

4.2.3 Flow in the SS Mode

Substituting the expressions for h , J_E , J_I , R , and θ given by (2.8), (2.32), (2.44), (3.4), and (3.16) respectively, into (2.20), and evaluating the integral, Q is given by (4.1) in the CR phase for $0 \leq t \leq t^*$ and

$$Q = \frac{2(\mathcal{E}R + 2\mathcal{I}\theta^*)}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{1/2} - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right) \right] \quad (4.31)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and hence from (2.19) $\bar{u}$ is given by (4.2) in the CR phase for $0 \leq t \leq t^*$ and

$$\bar{u} = \frac{4(\mathcal{E}R + 2\mathcal{I}\theta^*)}{\pi R\theta^*r} \left[\left(1 - \frac{r^2}{R^2}\right)^{-1/2} - \left(1 + \frac{r^2}{3R^2}\right) \right] \quad (4.32)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$. Evaluating (2.21) using (4.1) and (4.31), u and w are given by (4.3) and (4.4) in the CR phase for $0 \leq t \leq t^*$ and

$$u = \frac{24(\mathcal{E}R + 2\mathcal{I}\theta^*)z}{\pi r\theta^*R^3 \left(1 - \frac{r^2}{R^2}\right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right] \left[\theta^*R \left(1 - \frac{r^2}{R^2}\right) - z \right] \quad (4.33)$$

and

$$\begin{aligned} w = & \frac{8(\mathcal{E}R + 2\mathcal{I}\theta^*)z^2}{\pi\theta^*R^5 \left(1 - \frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\ & \left. + \theta^*R \left(1 - \frac{r^2}{R^2}\right) \left(-\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right) \right] - \frac{4\mathcal{I}\theta^*}{\pi R^2 \left(1 - \frac{r^2}{R^2}\right)^{1/2}} \end{aligned} \quad (4.34)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, while evaluating (2.37) using (2.43) U and W are given by (4.5) and (4.6) in the CR phase for $0 \leq t \leq t^*$ and

$$U = \frac{8\mathcal{I}\theta^* \left(\frac{R+r}{[(R+r)^2 + z^2]^{1/2}} - \frac{R-r}{[(R-r)^2 + z^2]^{1/2}} \right)}{\pi\varphi d_{\text{CA}} (d_{\text{CA}}^2 - 4R^2)^{1/2}} \quad (4.35)$$

and

$$W = \frac{8\mathcal{I}\theta^* z^s \left(\frac{1}{[(R+r)^2 + z^2]^{1/2}} - \frac{1}{[(R-r)^2 + z^2]^{1/2}} \right)}{\pi\varphi d_{\text{CA}} (d_{\text{CA}}^2 - 4R^2)^{1/2}} \quad (4.36)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$. For a droplet undergoing pure evaporation Q is given by (4.8) in the CR phase for $0 \leq t \leq t^*$ and (4.23) in the CA phase for $t^* < t \leq t_{\text{SS}}$,

and hence from (2.19) $\bar{u}$ is given by (4.9) in the CR phase for $0 \leq t \leq t^*$ and

$$\bar{u} = \frac{4}{\pi\theta^*r} \left[\left(1 - \frac{r^2}{R^2}\right)^{-1/2} - \left(1 + \frac{r^2}{3R^2}\right) \right] \quad (4.37)$$

in the CA phase for $t^* < t \leq t_{SS}$. Evaluating (2.21) using (4.8) and (4.23), u and w are given by (4.10) and (4.11) in the CR phase for $0 \leq t \leq t^*$ and

$$u = \frac{24z}{\pi r\theta^*3R^2 \left(1 - \frac{r^2}{R^2}\right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right] \left[\theta^*R \left(1 - \frac{r^2}{R^2}\right) - z \right] \quad (4.38)$$

and

$$w = \frac{8z^2}{\pi\theta^*3R^4 \left(1 - \frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\ \left. + \theta^*R \left(1 - \frac{r^2}{R^2}\right) \left(-\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right) \right] \quad (4.39)$$

in the CA phase for $t^* < t \leq t_{SS}$, while $U = W \equiv 0$ in the CR phase and CA phase, respectively (see D'Ambrosio *et al.* [84]). For a droplet undergoing pure imbibition Q is given by (4.12) in the CR phase for $0 \leq t \leq t^*$ and

$$Q = \frac{4\theta^*}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{1/2} - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right) \right] \quad (4.40)$$

in the CA phase for $t^* < t \leq t_{SS}$, and hence from (2.19) $\bar{u}$ is given by (4.13) in the CR phase for $0 \leq t \leq t^*$ and

$$\bar{u} = \frac{8}{\pi Rr} \left[\left(1 - \frac{r^2}{R^2}\right)^{-1/2} - \left(1 + \frac{r^2}{3R^2}\right) \right] \quad (4.41)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$. Evaluating (2.21) using (4.12) and (4.40), u and w are given by (4.14) and (4.15) in the CR phase for $0 \leq t \leq t^*$ and

$$u = \frac{48z}{\pi r \theta^{*2} R^3 \left(1 - \frac{r^2}{R^2}\right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right] \left[\theta^* R \left(1 - \frac{r^2}{R^2}\right) - z \right] \quad (4.42)$$

and

$$w = \frac{16z^2}{\pi \theta^{*2} R^5 \left(1 - \frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\ \left. + \theta^* R \left(1 - \frac{r^2}{R^2}\right) \left(-\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right) \right] - \frac{4\mathcal{I}\theta^*}{\pi R^2 \left(1 - \frac{r^2}{R^2}\right)^{1/2}} \quad (4.43)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, while U and W are given by (4.5) and (4.6) in the CR phase for $0 \leq t \leq t^*$, and by (4.20) and (4.21) in the CA phase for $t^* < t \leq t_{\text{SS}}$, with $\mathcal{I} = 1$.

We note that the flow within the droplet and the substrate in the CR and CA phases of the SS mode are qualitatively similar to those in the CR and CA modes, as discussed in Sections 4.2.2 and 4.2.3, respectively. Figures 4.7 and 4.8 shows the evolutions of Q and $\bar{u}$ as functions of r for several R and θ values, when $\theta^* = 1/2$, for (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure imbibition. In particular, Figures 4.7 and 4.8 illustrate that the mean flow within the droplet resembles that in the CR mode in the CR phase and that in the CA mode in the CA phase, respectively. The flow transition between the CR and the CA phase originates from the de-pinning of the contact line in the CA phase, as discussed in Section 2.5.

4.2.4 Flow in the SJ Mode

Substitution of the expressions for h , J_E , J_I , R , and θ given by (2.8), (2.32), (2.44), and (3.24) respectively, into (2.20), and evaluating the integral, Q in the n th CR phase

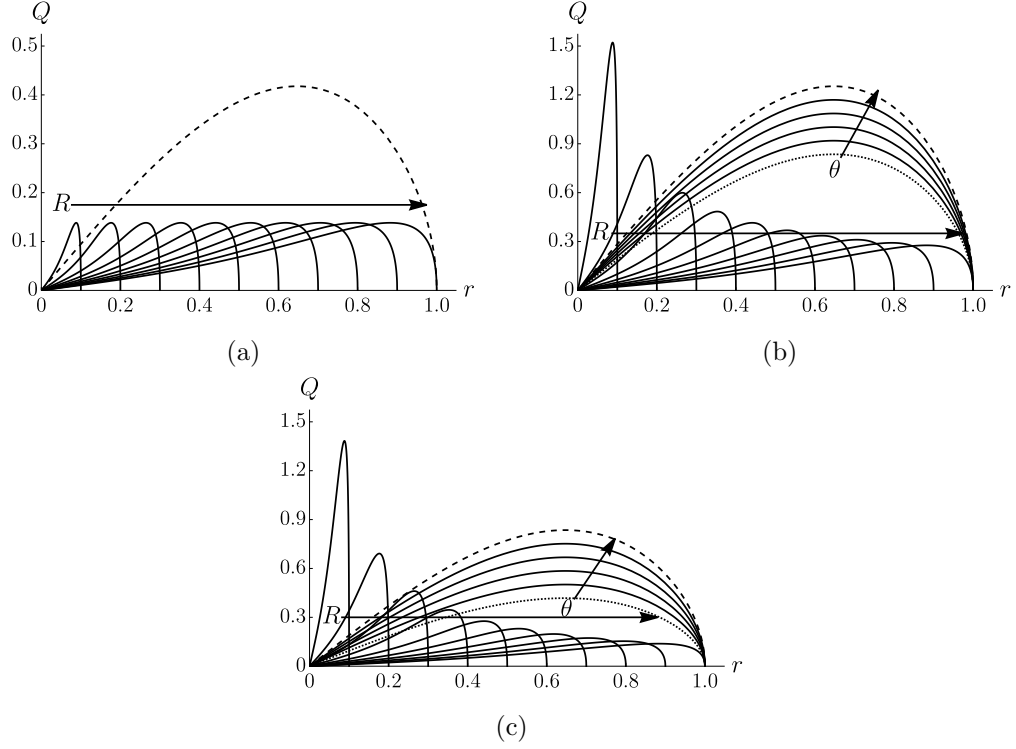


Figure 4.7: Q given by (4.1) and (4.31) in the SS mode plotted as functions of r for $\theta = 3/5, 7/10, \dots, 9/10$ in the CR phase and $R = 1/10, 2/5, \dots, 9/10$ in the CA phase when $\theta^* = 1/2$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed lines indicate the initial profile of Q at $\theta = 1$ (i.e., at $t = 0$), the dotted lines indicate the profile of Q at $\theta = \theta^* = 1/2$ (i.e., at $t = t^*$), and the arrows indicate the directions of increasing R and θ .

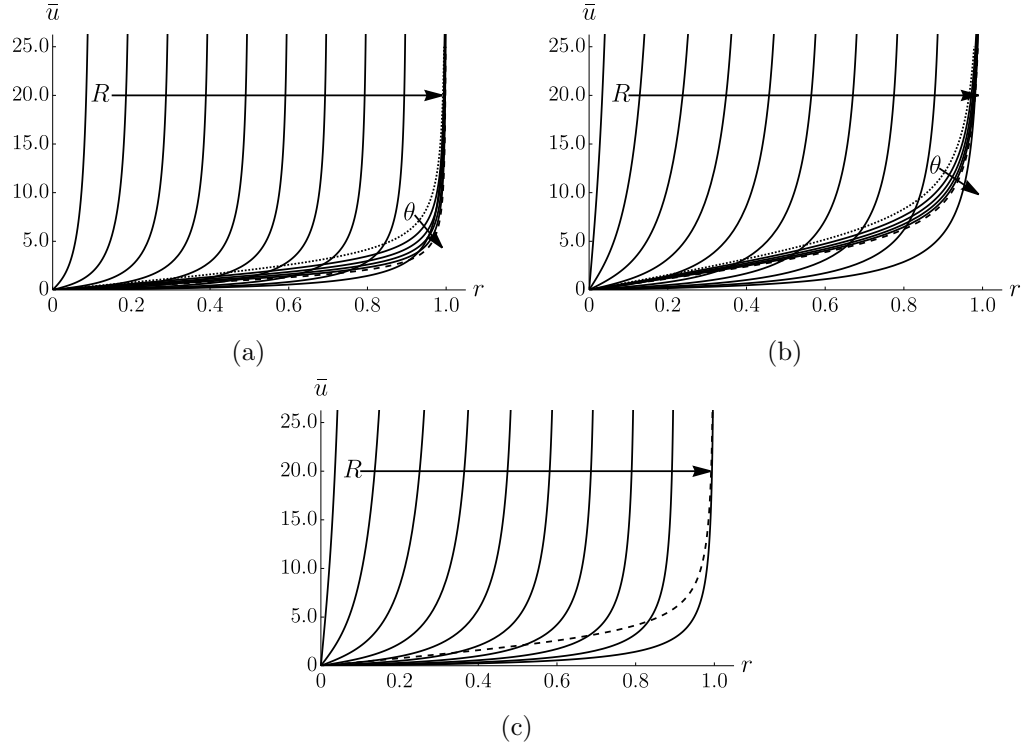


Figure 4.8: $\bar{u}$ given by (4.2) and (4.32) in the SS mode plotted as functions of r for $\theta = 3/5, 7/10, \dots, 9/10$ in the CR phase and $R = 1/10, 2/5, \dots, 9/10$ in the CA phase when $\theta^* = 1/2$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed lines indicate the initial profile of $\bar{u}$ at $\theta = 1$ (i.e., at $t = 0$), the dotted lines indicate the profile of $\bar{u}$ at $\theta = \theta^* = 1/2$ (i.e., at $t = t^*$), and the arrows indicate the directions of increasing R and θ .

is given by

$$Q = \frac{2(\mathcal{E}R_n + 2\mathcal{I}\theta)}{\pi r} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{1/2} - \left(1 - \frac{r^2}{R_n^2}\right)^2 \right] \quad (4.44)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and hence from (2.19) $\bar{u}$ in the n th CR phase is given by

$$\bar{u} = \frac{4(\mathcal{E}R_n + 2\mathcal{I}\theta)}{\pi\theta r R_n} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{-1/2} - \left(1 - \frac{r^2}{R_n^2}\right) \right] \quad (4.45)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Evaluating (2.21) using (4.44) u and w in the n th CR phase are given by

$$u = \frac{24(\mathcal{E}R_n + 2\mathcal{I}\theta)z}{\pi\theta^3 R_n^3 r \left(1 - \frac{r^2}{R_n^2}\right)^{5/2}} \left[1 - \left(1 - \frac{r^2}{R_n^2}\right)^{3/2} \right] \left[\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) - z \right] \quad (4.46)$$

and

$$w = \frac{4(\mathcal{E}R_n + 2\mathcal{I}\theta)z^2}{\pi\theta^3 R_n^5 \left(1 - \frac{r^2}{R_n^2}\right)^{7/2}} \left[\left\{ 10 - 4 \left(1 - \frac{r^2}{R_n^2}\right)^{3/2} \right\} z - 9\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) \right] - \frac{4\mathcal{I}\theta}{\pi R_n^2 \left(1 - \frac{r^2}{R_n^2}\right)^{1/2}} \quad (4.47)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while evaluating (2.37) using (2.43) U and W in the n th CR phase are given by

$$U = \frac{8\mathcal{I}\theta \left(\frac{R_n+r}{[(R_n+r)^2+z^2]^{1/2}} - \frac{R_n-r}{[(R_n-r)^2+z^2]^{1/2}} \right)}{\pi\varphi d_{\text{SJ}} (d_{\text{SJ}}^2 - 4R_n^2)^{1/2}} \quad (4.48)$$

and

$$W = \frac{8\mathcal{I}\theta z^8 \left(\frac{1}{[(R_n+r)^2+z^2]^{1/2}} - \frac{1}{[(R_n-r)^2+z^2]^{1/2}} \right)}{\pi\varphi d_{\text{SJ}} (d_{\text{SJ}}^2 - 4R_n^2)^{1/2}} \quad (4.49)$$

Chapter 4. Flow Within the Droplet and the Substrate

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), where we have introduced the notation

$$d_{SJ} = [(R_n + r)^2 + z^{s2}]^{1/2} + [(R_n - r)^2 + z^{s2}]^{1/2}. \quad (4.50)$$

For a droplet undergoing pure evaporation Q in the n th CR phase is given by

$$Q = \frac{2R_n}{\pi r} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{1/2} - \left(1 - \frac{r^2}{R_n^2}\right)^2 \right] \quad (4.51)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and hence from (2.19) $\bar{u}$ in the n th CR phase is given by

$$\bar{u} = \frac{4}{\pi \theta r} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{-1/2} - \left(1 - \frac{r^2}{R_n^2}\right) \right] \quad (4.52)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Evaluating (2.21) using (4.51) u and w in the n th CR phase are given by

$$u = \frac{24z}{\pi \theta^3 R_n^2 r \left(1 - \frac{r^2}{R_n^2}\right)^{5/2}} \left[1 - \left(1 - \frac{r^2}{R_n^2}\right)^{3/2} \right] \left[\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) - z \right] \quad (4.53)$$

and

$$w = \frac{4z^2}{\pi \theta^3 R_n^4 \left(1 - \frac{r^2}{R_n^2}\right)^{7/2}} \left[\left\{ 10 - 4 \left(1 - \frac{r^2}{R_n^2}\right)^{3/2} \right\} z - 9\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) \right] \quad (4.54)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while $U = W \equiv 0$ in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) (see D'Ambrosio *et al.* [84]). For a droplet undergoing pure imbibition Q in the n th CR phase is given by

$$Q = \frac{4\theta}{\pi r} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{1/2} - \left(1 - \frac{r^2}{R_n^2}\right)^2 \right] \quad (4.55)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and hence from (2.19) $\bar{u}$ in the n th CR phase is given by

$$\bar{u} = \frac{8}{\pi r R_n} \left[\left(1 - \frac{r^2}{R_n^2} \right)^{-1/2} - \left(1 - \frac{r^2}{R_n^2} \right) \right] \quad (4.56)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Evaluating (2.21) using (4.55) u and w in the n th CR phase are given by

$$u = \frac{48z}{\pi \theta^2 R_n^3 r \left(1 - \frac{r^2}{R_n^2} \right)^{5/2}} \left[1 - \left(1 - \frac{r^2}{R_n^2} \right)^{3/2} \right] \left[\theta R_n \left(1 - \frac{r^2}{R_n^2} \right) - z \right] \quad (4.57)$$

and

$$\begin{aligned} w = & \frac{8z^2}{\pi \theta^2 R_n^5 \left(1 - \frac{r^2}{R_n^2} \right)^{7/2}} \left[\left\{ 10 - 4 \left(1 - \frac{r^2}{R_n^2} \right)^{3/2} \right\} z - 9\theta R_n \left(1 - \frac{r^2}{R_n^2} \right) \right] \\ & - \frac{4\theta}{\pi R_n^2 \left(1 - \frac{r^2}{R_n^2} \right)^{1/2}} \end{aligned} \quad (4.58)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while U and W in the n th CR phase are given by (4.48) and (4.49) with $\mathcal{I} = 1$, for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$).

We note that the flow within the droplet and the substrate in the n th CR phase of the SJ mode is qualitatively similar to that in the CR mode, as discussed in Section 4.2.1. Figures 4.9 and 4.10 show the evolutions of Q and $\bar{u}$ as functions of r in several CR phases for (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure imbibition, when $\theta_{\min} = 1/2$. In particular, Figures 4.9 and 4.10 illustrate that the behaviour of the mean flow within the droplet resembles that of the CR mode in the n th CR phase, as discussed in Section 4.2.1.

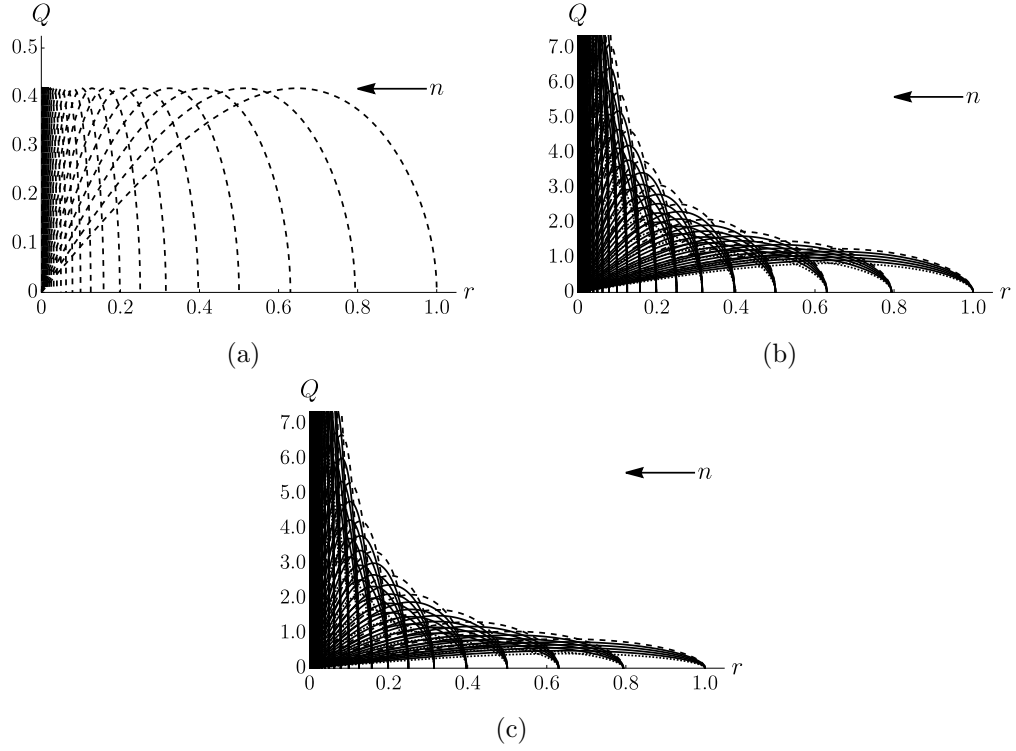


Figure 4.9: Q given by (4.44) in the SJ mode plotted as functions of r at $\theta = 3/5, 7/10, 4/5, 9/10$ in each CR phase when $\theta_{\min} = 1/2$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed and the dotted lines indicate the values at $t = t_{n-1}$ and $t = t_n$ ($n = 1, 2, 3, \dots$) (i.e., at the start and the end of each CR phase) corresponding to $\theta = \theta_{\max} = 1$ and $\theta = \theta_{\min} = 1/2$, respectively, and the arrows indicate the directions of increasing n .

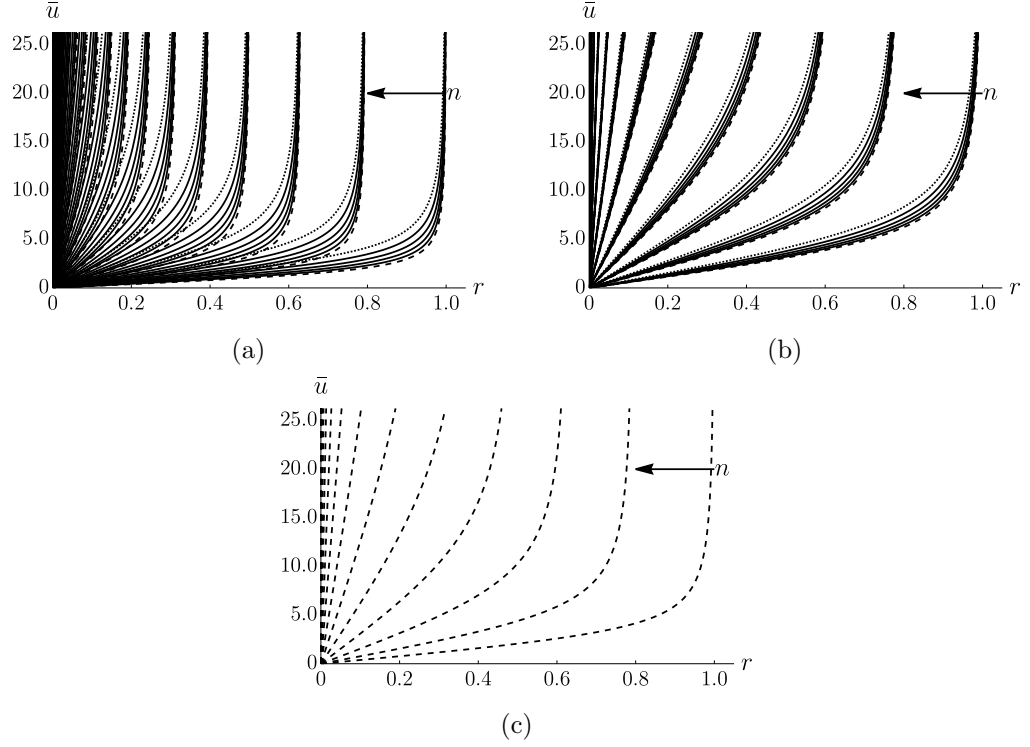


Figure 4.10: $\bar{u}$ given by (4.45) in the SJ mode plotted as functions of r at $\theta = 3/5, 7/10, 4/5, 9/10$ in each CR phase when $\theta_{\min} = 1/2$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition. The dashed and the dotted lines indicate the values at t_{n-1} and $t = t_n$ ($n = 1, 2, 3, \dots$) (i.e., at the start and the end of each CR phase) corresponding to $\theta = \theta_{\max} = 1$ and $\theta = \theta_{\min} = 1/2$, respectively, and the arrows indicate the directions of increasing n .

4.3 Spatially Uniform Local Imbibition Mass Flux

4.3.1 Flow in the CR Mode

Substituting the expressions for h , J_E , J_I , R , and θ given by (2.8), (2.32), (2.57) or (2.65), and (3.39) or (3.75) respectively, into (2.20), and evaluating the integral, Q is given by

$$Q = \frac{2\mathcal{E}}{\pi r} \left[(1-r^2)^{1/2} - (1-r^2)^2 \right] + \frac{\mathcal{I}J_I r (1-r^2)}{2}, \quad (4.59)$$

and hence from (4.59) $\bar{u}$ is given by

$$\bar{u} = \frac{4\mathcal{E}}{\pi r \theta} \left[(1-r^2)^{-1/2} - (1-r^2) \right] + \frac{\mathcal{I}J_I r}{\theta}. \quad (4.60)$$

Evaluating (2.21) using (4.59) u and w are given by

$$u = \frac{24\mathcal{E}z}{\pi\theta^3 r (1-r^2)^{5/2}} \left[1 - (1-r^2)^{3/2} \right] [\theta(1-r^2) - z] + \frac{6\mathcal{I}J_I r z \{ \theta(1-r^2) + z \}}{\theta^3 (1-r^2)^2} \quad (4.61)$$

and

$$w = \frac{4\mathcal{E}z^2}{\pi\theta^3 (1-r^2)^{7/2}} \left[\left\{ 10 - 4(1-r^2)^{3/2} \right\} z - 9\theta(1-r^2) \right] + \mathcal{I}J_I \left[-1 - \frac{6z^2}{\theta^2 (1-r^2)^2} + \frac{4(1+r^2)z^3}{\theta^3 (1-r^2)^3} \right], \quad (4.62)$$

while W is given by

$$W = -\frac{\mathcal{I}J_I}{\varphi}. \quad (4.63)$$

In contrast to Section 4.2, Q , $\bar{u}$, u , and $w + \mathcal{I}J_I$ do not depend on $\mathcal{E}$ and $\mathcal{I}$ in the combination of $\mathcal{E} + 2\mathcal{I}\theta$. However, W depends linearly on $\mathcal{I}J_I$ but only depends on $\mathcal{E}$ through θ or t dependence. Inspection of (4.59), (4.60), (4.61), and (4.62) reveals that $Q \geq 0$, $\bar{u} \geq 0$, $u \geq 0$, and $w \leq 0$ (i.e., the flow is always outwards and downwards in both

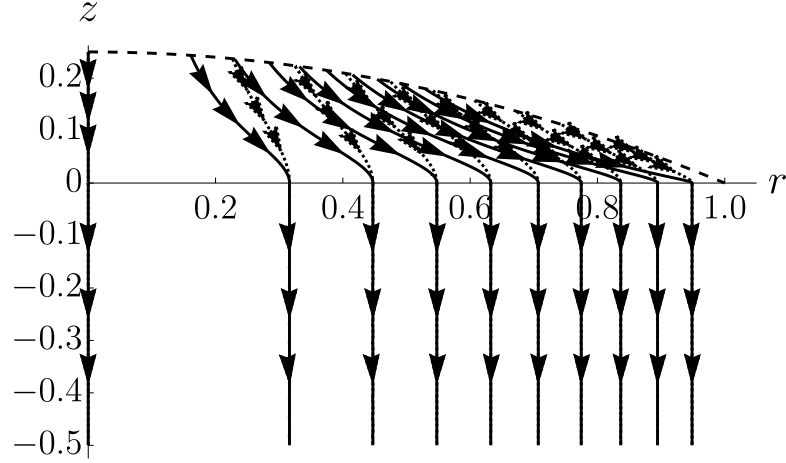


Figure 4.11: Instantaneous streamlines of the flow within the droplet and the substrate for a droplet evolving in the CR mode calculated from (4.61), (4.62), and (4.63) with J_I given by (2.57) for simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid lines) and pure imbibition (dotted lines), when $\theta = 1/2$.

the droplet and the substrate). We also find that, in the same manner as that discussed in Section 4.2, the flow within the droplet is the sum of the evaporation and imbibition contributions. In particular, we find that $Q = O(r) \rightarrow 0^+$ and $\bar{u} = O(r) \rightarrow 0^+$ as $r \rightarrow 0^+$ and $Q = O((1-r)^{1/2}) \rightarrow 0^+$ and $\bar{u} = O((1-r)^{-1/2}) \rightarrow \infty$ as $r \rightarrow 1^-$. Hence, the evaporation contribution to $\bar{u}$ dominates at the contact line. In particular, for a droplet undergoing pure imbibition with a spatially uniform imbibition flux $Q = O(r) \rightarrow 0^+$ and $\bar{u} = O(r) \rightarrow 0^+$ as $r \rightarrow 0^+$ and $Q = O(1-r) \rightarrow 0^+$ and $\bar{u} = O(1) = \mathcal{I}J_I/\theta$ as $r \rightarrow 1^-$. Figure 4.11 shows instantaneous streamlines of the flow for a droplet evolving in the CR mode calculated from equations (4.61), (4.62), and (4.63) when J_I is given by (2.57) for simultaneous evaporation and imbibition (solid lines) and pure imbibition (dotted lines), all for the same value of θ . Note that, because they are for the same value θ , the flow within the substrate is identical for the two situations shown in Figure 4.11. We note that the plots of Q and $\bar{u}$ in the CR mode are similar to those given in Section 4.2.1 and so are not included. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate Q is given by

$$Q = \frac{2r(1-r^2)}{1-\theta}, \quad (4.64)$$

Chapter 4. Flow Within the Droplet and the Substrate

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{4r}{\theta(1-\theta)}. \quad (4.65)$$

Evaluating (2.21) using (4.64) u and w are given by

$$u = \left[\frac{24rz \{ \theta (1-r^2) + z \}}{\theta^3(1-\theta)(1-r^2)^2} \right] \quad (4.66)$$

and

$$w = \frac{4}{1-\theta} \left[-1 - \frac{6z^2}{\theta^2(1-r^2)^2} + \frac{4(1+r^2)z^3}{\theta^3(1-r^2)^3} \right], \quad (4.67)$$

while evaluating (4.63) using (2.57) W is given by

$$W = -\frac{4}{\varphi(1-\theta)}. \quad (4.68)$$

Inspection of (4.65) reveals that $\bar{u} = O(1) = 4/(\theta(1-\theta))$ as $r \rightarrow 1^-$ and, hence, is unimodal in terms of θ . Figure 4.12 shows $\bar{u}(1, t)$ given by (4.65) as a function of θ . In particular, Figure 4.12 illustrates that $\bar{u} \rightarrow \infty$ as $\theta \rightarrow 0^+$ and $\theta \rightarrow 1^-$, respectively. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate Q is given by

$$Q = \theta r (1-r^2), \quad (4.69)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = 2r. \quad (4.70)$$

Evaluating (2.21) using (4.69) u and w are given by

$$u = \frac{12rz [\theta (1-r^2) + z]}{\theta^2 (1-r^2)^2} \quad (4.71)$$

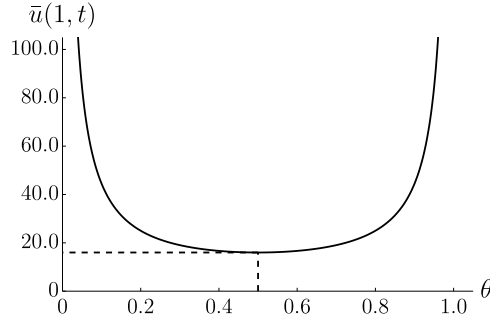


Figure 4.12: $\bar{u}(1, t)$ given by (4.65) in the CR mode as a function of θ . The dashed lines indicate the minimum value of $\bar{u}(1, t) = 16$ that occurs at $\theta = 1/2$.

and

$$w = 2\theta \left[-1 - \frac{6z^2}{\theta^2 (1-r^2)^2} + \frac{4(1+r^2)z^3}{\theta^3 (1-r^2)^3} \right], \quad (4.72)$$

while evaluating (4.63) using (2.65) W is given by

$$W = -\frac{2\theta}{\varphi}. \quad (4.73)$$

Inspection of (4.70) reveals that $\bar{u} = O(1) = 2^-$ as $r \rightarrow 1^-$ and hence, in contrast to a finitely thick, anisotropic, initially dry, porous substrate, $\bar{u}$ given by (4.65), is constant (in time) as the droplet evolves. The physical reason for this is that Q , given by (4.69), decreases with θ in the same manner as h and, hence, the mean flow within the droplet remains constant as the droplet evolves.

4.3.2 Flow in the CA Mode

Substituting the expressions for h , J_E , J_I , R , and θ given by (2.8), (2.32), (2.57), (3.43) respectively, into (2.20), and evaluating the integral, Q is given by

$$Q = \frac{2\mathcal{E}R}{\pi r} \left[\left(1 - \frac{r^2}{R^2}\right)^{1/2} - \left(1 + \frac{r^2}{3R^2}\right) \left(1 - \frac{r^2}{R^2}\right) \right] - \frac{\mathcal{I}J_I r \left(1 - \frac{r^2}{R^2}\right)}{6}, \quad (4.74)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = \frac{4\mathcal{E}}{\pi r} \left[\left(1 - \frac{r^2}{R^2} \right)^{-1/2} - \left(1 + \frac{r^2}{3R^2} \right) \right] - \frac{\mathcal{I}J_I r}{3R}. \quad (4.75)$$

Evaluating (2.21) using (4.74) u and w are given by

$$\begin{aligned} u = & \frac{24\mathcal{E}z}{\pi R^2 r \left(1 - \frac{r^2}{R^2} \right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2} \right) \left(1 - \frac{r^2}{R^2} \right)^{1/2} \right] \left[R \left(1 - \frac{r^2}{R^2} \right) - z \right] \\ & - \frac{2\mathcal{I}J_I r z \left\{ R \left(1 - \frac{r^2}{R^2} \right) - z \right\}}{R^3 \left(1 - \frac{r^2}{R^2} \right)^2} \end{aligned} \quad (4.76)$$

and

$$\begin{aligned} w = & \frac{8\mathcal{E}z^2}{\pi R^4 \left(1 - \frac{r^2}{R^2} \right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2} \right)^{1/2} \left(7 + \frac{r^2}{R^2} \right) \right\} z \right. \\ & \left. + R \left(1 - \frac{r^2}{R^2} \right) \left\{ -\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2} \right)^{1/2} \right\} \right] \\ & + \mathcal{I}J_I \left[-1 + \frac{2z^2}{R^2 \left(1 - \frac{r^2}{R^2} \right)^2} - \frac{4z^3 \left(1 + \frac{r^2}{R^2} \right)}{3R^3 \left(1 - \frac{r^2}{R^2} \right)^3} \right], \end{aligned} \quad (4.77)$$

while W is given by (4.63).

Note that, in contrast to Section 4.2.2, Q , $\bar{u}$, u , and $w + \mathcal{I}J_I$ do not depend on $\mathcal{E}$ and $\mathcal{I}$ in the combination of $\mathcal{E}R + 2\mathcal{I}$. However, W depends linearly on $\mathcal{I}J_I$ but only depends on $\mathcal{E}$ through R or t dependence. On one hand, inspection of (4.74), (4.75), (4.76), and (4.77) reveals that the evaporation contribution to the flow $Q \geq 0$, $\bar{u} \geq 0$, $u \geq 0$, and $w \leq 0$ (i.e., the evaporation contribution to the flow is always outwards and downwards in both the droplet and the substrate). On the other hand, inspection of (4.74), (4.75), (4.76), and (4.77) reveals that the imbibition contribution to the flow $Q \leq 0$, $\bar{u} \leq 0$, $u \leq 0$, and $w \leq 0$ (i.e., the imbibition contribution to the flow is always inwards and downwards in both the droplet and the substrate). Hence,

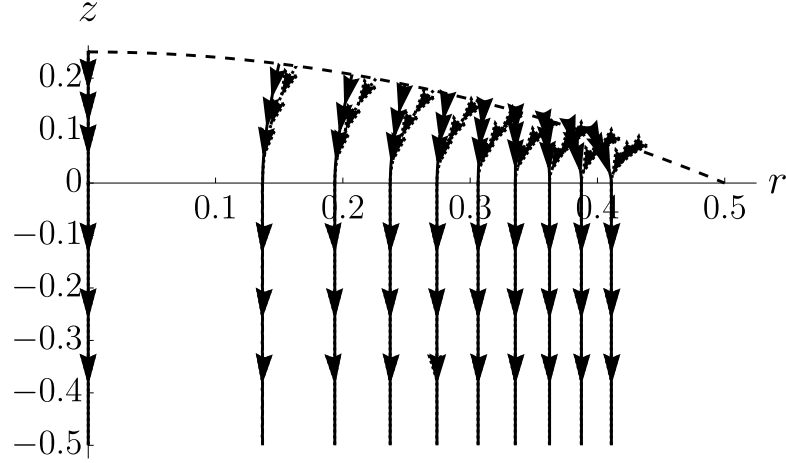


Figure 4.13: Instantaneous streamlines of the flow within the droplet and the substrate for a droplet evolving in the CA mode calculated from (4.76), (4.77), and (4.63) with J_I given by (2.57) for simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid lines) and pure imbibition (dotted lines), when $R = 1/2$.

a droplet undergoing simultaneous evaporation and imbibition (in situations where the local mass imbibition flux is spatially uniform) will experience regions of outwards, inwards, and zero flow. In particular, we find that $Q = O(r) \rightarrow 0^+$ and $\bar{u} = O(r) \rightarrow 0^+$ as $r \rightarrow 0^+$ and $Q = O((R-r)^{1/2}) \rightarrow 0^+$ and $\bar{u} = O((R-r)^{-1/2}) \rightarrow \infty$ as $r \rightarrow R^-$. Hence, the evaporation contribution to $\bar{u}$ dominates at the contact line and the flow is always outwards as $r \rightarrow R^-$. In particular, for a droplet undergoing pure imbibition with a spatially uniform imbibition flux $Q = O(r) = -\mathcal{I}J_I r/6 \rightarrow 0^-$ and $\bar{u} = O(r) = -\mathcal{I}J_I r/(3R) \rightarrow 0^-$ and $Q = O(R-r) = -\mathcal{I}J_I(R-r)/3 \rightarrow 0^-$ and $\bar{u} = O(1) = -\mathcal{I}J_I/3$ as $r \rightarrow R^-$. Figure 4.13 shows the instantaneous streamlines of the flow for a droplet evolving in the CA mode calculated from equations (4.6), (4.76), and (4.77) when J_I is given by (2.57) for simultaneous evaporation and imbibition (solid lines) and pure imbibition (dotted lines), all for the same value of R . In particular, Figure 4.13 illustrates that the flow within the droplet has outwards and inwards components for simultaneous evaporation and imbibition and is always inwards for pure imbibition. Note that, because they are for the same value of R , the flow within the substrate is identical for the two situations shown in Figure 4.13. We note that the instantaneous streamlines for a droplet undergoing simultaneous evaporation and imbibition on a

finitely thick, anisotropic, flooded, porous substrate are qualitatively similar to those shown in Figure 4.13. Furthermore, the plots of Q and $\bar{u}$ in the CA mode are similar to those discussed in Section 4.2.2 and, hence, are not included. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate Q is given by

$$Q = -\frac{2r \left(1 - \frac{r^2}{R^2}\right)}{9(1-R)}, \quad (4.78)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = -\frac{4r}{9R(1-R)}. \quad (4.79)$$

Evaluating (2.21) using (4.78) u and w are given by

$$u = -\frac{8rz \left[R \left(1 - \frac{r^2}{R^2}\right) - z \right]}{3R^3(1-R) \left(1 - \frac{r^2}{R^2}\right)^2} \quad (4.80)$$

and

$$w = \frac{4}{3(1-R)} \left[-1 + \frac{2z^2}{R^2 \left(1 - \frac{r^2}{R^2}\right)^2} - \frac{4z^3 \left(1 + \frac{r^2}{R^2}\right)}{3R^3 \left(1 - \frac{r^2}{R^2}\right)^3} \right], \quad (4.81)$$

while evaluating (4.63) using (2.57) W is given by

$$W = -\frac{4(1-R)}{3\varphi}. \quad (4.82)$$

For a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate Q is given by

$$Q = -\frac{r \left(1 - \frac{r^2}{R^2}\right)}{3R}, \quad (4.83)$$

and hence from (2.19) $\bar{u}$ is given by

$$\bar{u} = -\frac{2r}{3R^2}. \quad (4.84)$$

Evaluating (2.21) using (4.83) u and w are given by

$$u = -\frac{4rz \left[R \left(1 - \frac{r^2}{R^2} \right) - z \right]}{R^4 \left(1 - \frac{r^2}{R^2} \right)^2} \quad (4.85)$$

and

$$w = \frac{2}{R} \left[-1 + \frac{2z^2}{R^2 \left(1 - \frac{r^2}{R^2} \right)^2} - \frac{4z^3 \left(1 + \frac{r^2}{R^2} \right)}{3R^3 \left(1 - \frac{r^2}{R^2} \right)^3} \right], \quad (4.86)$$

while evaluating (4.63) using (2.65) W is given by

$$W = -\frac{2}{\varphi R}. \quad (4.87)$$

Inspection of (4.79) reveals that $\bar{u} = O(1) = -4/(9(1-R))$ as $r \rightarrow R^-$. In contrast, inspection of (4.84) reveals that $\bar{u} = O(1) = -2/(3R)$ as $r \rightarrow R^-$. Figure 4.14 shows $\bar{u}(R, t)$ as a function of R for a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate (dotted line) and a finitely thick, anisotropic, flooded, porous substrate (solid line). In particular, Figure 4.14 illustrates that the flow at the centre and the contact line within the droplet have opposing behaviours on both substrates, and that $\bar{u}$ at the contact line is equal on both substrates when $R = 0.6$ and $\bar{u} \simeq -1.1111$. Here the principal difference is that a pinned contact line produces an outward flow, whereas a moving contact-line generates an inward flow, leading to qualitatively different flow profiles in the CR and CA modes.

4.3.3 Flow in the SS Mode

Substituting the expressions for h , J_E , R , and θ given by (2.8), (2.32), (2.57), (3.39), and (3.49) respectively, into (2.20), and evaluating the integral, Q in the SS mode is

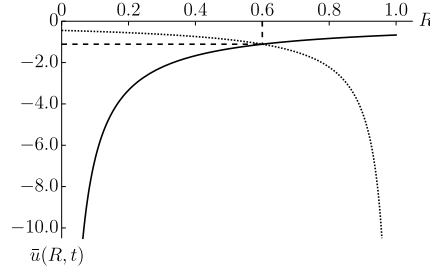


Figure 4.14: $\bar{u}(R, t)$ given by (4.79) (dotted line) and (4.84) (solid line) in the CA mode as functions of R . The dashed lines indicate the value of $\bar{u}(R, t) \simeq -1.1111$ where both a finitely thick, anisotropic, dry and flooded, porous substrate yield the same value of $\bar{u}$ that occurs at $R = 3/5$.

given by (4.59) in the CR phase for $0 \leq t \leq t^*$ and by (4.74) in the CA phase for $t^* < t \leq t_{\text{SS}}$, and hence from (2.19) $\bar{u}$ is given by (4.60) in the CR phase for $0 \leq t \leq t^*$ and by

$$\bar{u} = \frac{4\mathcal{E}}{\pi r \theta^*} \left[\left(1 - \frac{r^2}{R^2} \right)^{-1/2} - \left(1 + \frac{r^2}{3R^2} \right) \right] - \frac{\mathcal{I} J_{\text{I}} r}{3\theta^* R} \quad (4.88)$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$. Evaluating (2.21) using (4.59) and (4.74), u and w are given by (4.61) and (4.62) in the CR phase for $0 \leq t \leq t^*$ and

$$u = \frac{24\mathcal{E}z}{\pi r \theta^{*3} R^2 \left(1 - \frac{r^2}{R^2} \right)^{5/2}} \left[1 - \left(1 + \frac{r^2}{3R^2} \right) \left(1 - \frac{r^2}{R^2} \right)^{1/2} \right] \left[\theta^* R \left(1 - \frac{r^2}{R^2} \right) - z \right] - \frac{2\mathcal{I} J_{\text{I}} r z \left\{ \theta^* R \left(1 - \frac{r^2}{R^2} \right) - z \right\}}{\theta^{*3} R^3 \left(1 - \frac{r^2}{R^2} \right)^2} \quad (4.89)$$

and

$$\begin{aligned}
 w = & \frac{8\mathcal{E}z^2}{\pi\theta^{*3}R^4\left(1-\frac{r^2}{R^2}\right)^{7/2}} \left[\left\{ 5 - \frac{2}{3} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \left(7 + \frac{r^2}{R^2}\right) \right\} z \right. \\
 & + \theta^* R \left(1 - \frac{r^2}{R^2}\right) \left\{ -\frac{9}{2} + 4 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \right\} \left. \right] \\
 & + \mathcal{I}J_I \left[-1 + \frac{2z^2}{\theta^{*2}R^2\left(1-\frac{r^2}{R^2}\right)^2} - \frac{4z^3\left(1+\frac{r^2}{R^2}\right)}{3\theta^{*3}R^3\left(1-\frac{r^2}{R^2}\right)^3} \right], \tag{4.90}
 \end{aligned}$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, while W is given by (4.63) in the CR phase and the CR phase, respectively. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate Q is given by (4.64) in the CR phase for $0 \leq t \leq t^*$ and

$$Q = -\frac{2r\left(1-\frac{r^2}{R^2}\right)}{3[3\theta^*(1-R)+1-\theta^*]} \tag{4.91}$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$, and hence from (2.19) $\bar{u}$ is given by (4.65) in the CR phase for $0 \leq t \leq t^*$ and

$$\bar{u} = -\frac{4r}{3\theta^*R[3\theta^*(1-R)+1-\theta^*]} \tag{4.92}$$

in the CA phase for $t^* < t \leq t_{\text{SS}}$. Evaluating (2.21) using (4.64) and (4.91), u and w are given by (4.66) and (4.67) in the CR phase for $0 \leq t \leq t^*$ and

$$u = -\frac{8rz\left[\theta^*R\left(1-\frac{r^2}{R^2}\right)-z\right]}{\theta^{*3}R^3[3\theta^*(1-R)+1-\theta^*]\left(1-\frac{r^2}{R^2}\right)^2} \tag{4.93}$$

and

$$w = \frac{4}{3\theta^*(1-R)+1-\theta^*} \left[-1 + \frac{2z^2}{\theta^{*2}R^2\left(1-\frac{r^2}{R^2}\right)^2} - \frac{4z^3\left(1+\frac{r^2}{R^2}\right)}{3\theta^{*3}R^3\left(1-\frac{r^2}{R^2}\right)^3} \right] \tag{4.94}$$

in the CA phase for $t^* < t \leq t_{SS}$, while W is given by (4.68) in the CR phase for $0 \leq t \leq t^*$ and

$$W = -\frac{4}{\varphi [3\theta^* (1 - R) + 1 - \theta^*]} \quad (4.95)$$

in the CA phase for $t^* < t \leq t_{SS}$. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate Q is given by (4.69) in the CR phase for $0 \leq t \leq t^*$ and

$$Q = -\frac{\theta^* r \left(1 - \frac{r^2}{R^2}\right)}{3R} \quad (4.96)$$

in the CA phase for $t^* < t \leq t_{SS}$, and hence from (2.19) $\bar{u}$ is given by (4.70) in the CR phase for $0 \leq t \leq t^*$ and by (4.84) in the CA phase for $t^* < t \leq t_{SS}$. Evaluating (2.21) using (4.69) and (4.96), u and w are given by (4.71) and (4.72) in the CR phase for $0 \leq t \leq t^*$ and

$$u = -\frac{4rz \left[\theta^* R \left(1 - \frac{r^2}{R^2}\right) - z \right]}{\theta^{*2} R^4 \left(1 - \frac{r^2}{R^2}\right)^2} \quad (4.97)$$

and

$$w = \frac{2\theta^*}{R} \left[-1 + \frac{2z^2}{\theta^{*2} R^2 \left(1 - \frac{r^2}{R^2}\right)^2} - \frac{4z^3 \left(1 + \frac{r^2}{R^2}\right)}{3\theta^{*3} R^3 \left(1 - \frac{r^2}{R^2}\right)^3} \right] \quad (4.98)$$

in the CA phase for $t^* < t \leq t_{SS}$, while W is given by (4.73) in the CR phase for $0 \leq t \leq t^*$ and

$$W = -\frac{2\theta^*}{\varphi R} \quad (4.99)$$

in the CA phase for $t^* < t \leq t_{SS}$.

We find that the behaviour of the flow within the droplet and the substrate in the CR and CA phases of the SS mode are qualitatively similar to that in the CR and CA

modes, as discussed in Sections 4.3.1 and 4.3.2, respectively.

4.3.4 Flow in the SJ Mode

Substituting the expressions for h , J_E , J_I , R , and θ given by (2.32), (2.57) or (2.65), and (3.54) or (3.88), respectively, into (2.20), and evaluating the integral, Q in the n th CR phase is given by

$$Q = \frac{2\mathcal{E}R_n}{\pi r} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{1/2} - \left(1 - \frac{r^2}{R_n^2}\right)^2 \right] + \frac{\mathcal{I}J_I r \left(1 - \frac{r^2}{R_n^2}\right)}{2} \quad (4.100)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and hence from (2.19) $\bar{u}$ in the n th CR phase is given by

$$\bar{u} = \frac{4\mathcal{E}}{\pi\theta r} \left[\left(1 - \frac{r^2}{R_n^2}\right)^{-1/2} - \left(1 - \frac{r^2}{R_n^2}\right) \right] + \frac{\mathcal{I}J_I r}{\theta R_n} \quad (4.101)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Evaluating (2.21) using (4.100) u and w in the n th CR phase are given by

$$\begin{aligned} u = & \frac{24\mathcal{E}z}{\pi\theta^3 R_n^2 r \left(1 - \frac{r^2}{R_n^2}\right)^{5/2}} \left[1 - \left(1 - \frac{r^2}{R_n^2}\right)^{3/2} \right] \left[\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) - z \right] \\ & + \frac{6\mathcal{I}J_I r z \left[\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) - z \right]}{\theta^3 R_n^3 \left(1 - \frac{r^2}{R_n^2}\right)^2} \end{aligned} \quad (4.102)$$

and

$$\begin{aligned} w = & \frac{4\mathcal{E}z^2}{\pi\theta^3 R_n^4 \left(1 - \frac{r^2}{R_n^2}\right)^{7/2}} \left[\left\{ 10 - 4 \left(1 - \frac{r^2}{R_n^2}\right)^{3/2} \right\} z - 9\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) \right] \\ & + \mathcal{I}J_I \left[-1 - \frac{6z^2}{\theta^2 R_n^2 \left(1 - \frac{r^2}{R_n^2}\right)^2} + \frac{4z^3 \left(1 + \frac{r^2}{R_n^2}\right)}{\theta^3 R_n^3 \left(1 - \frac{r^2}{R_n^2}\right)^3} \right] \end{aligned} \quad (4.103)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while W in the n th CR phase is given by (4.63) for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). For a droplet undergoing pure imbibition on a finitely

thick, anisotropic, initially dry, porous substrate Q in the n th CR phase is given by

$$Q = \frac{2r \left(1 - \frac{r^2}{R_n^2}\right)}{R_n (\theta_{\max} - \theta) + 4(2t_{n-1})^{1/2}} \quad (4.104)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and hence from (2.19) $\bar{u}$ in the n th CR phase is given by

$$\bar{u} = \frac{4r}{\theta R_n \left[R_n (\theta_{\max} - \theta) + 4(2t_{n-1})^{1/2} \right]} \quad (4.105)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Evaluating (2.21) using (4.104) u and w in the n th CR phase are given by

$$u = \frac{24rz \left[\theta R_n \left(1 - \frac{r^2}{R_n^2}\right) - z \right]}{\theta^3 R_n^3 \left[R_n (\theta_{\max} - \theta) + 4(2t_{n-1})^{1/2} \right] \left(1 - \frac{r^2}{R_n^2}\right)^2} \quad (4.106)$$

and

$$w = \frac{4}{R_n (\theta_{\max} - \theta) + 4(2t_{n-1})^{1/2}} \left[-1 - \frac{6z^2}{\theta^2 R_n^2 \left(1 - \frac{r^2}{R_n^2}\right)^2} + \frac{4z^3 \left(1 + \frac{r^2}{R_n^2}\right)}{\theta^3 R_n^3 \left(1 - \frac{r^2}{R_n^2}\right)^3} \right] \quad (4.107)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while W in the n th CR phase is given by

$$W = -\frac{4}{\varphi \left[R_n (\theta_{\max} - \theta) + 4(2t_{n-1})^{1/2} \right]} \quad (4.108)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). For a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate Q in the n th CR phase is given by

$$Q = \frac{\theta r \left(1 - \frac{r^2}{R_n^2}\right)}{R_n} \quad (4.109)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), and hence from (2.19) $\bar{u}$ in the n th CR phase is given by

$$\bar{u} = \frac{2r}{R_n^2} \quad (4.110)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Evaluating (2.21) using (4.109) u and w in the n th CR phase are given by

$$u = \frac{12rz \left[\theta R_n \left(1 - \frac{r^2}{R_n^2} \right) - z \right]}{\theta^2 R_n^4 \left(1 - \frac{r^2}{R_n^2} \right)^2} \quad (4.111)$$

and

$$w = \frac{2\theta}{R_n} \left[-1 - \frac{6z^2}{\theta^2 R_n^2 \left(1 - \frac{r^2}{R_n^2} \right)^2} + \frac{4z^3 \left(1 + \frac{r^2}{R_n^2} \right)}{\theta^3 R_n^3 \left(1 - \frac{r^2}{R_n^2} \right)^3} \right] \quad (4.112)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while W in the n th CR phase is given by

$$W = -\frac{2\theta}{\varphi R_n} \quad (4.113)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$).

We find that the behaviour of the flow within the droplet and the substrate in the n th CR phase of the SJ mode are qualitatively similar to that in the CR mode, as discussed in Section 4.3.1.

4.4 Conclusions

In Chapter 4 we have analysed mathematical models for the flow within the droplet and substrate on three different porous substrates in the CR, CA, SS, and SJ modes.

In Section 4.2 we determined the flow within the droplet and an infinitely thick, isotropic, flooded, porous substrate in the CR, CA, SS, and SJ modes, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.1, respectively.

We found that the flow within the droplet is the sum of the evaporation and imbibition contributions, and is always outwards and downwards in both the droplet and the substrate in the CR, CA, SS, and SJ modes.

In Section 4.3 we determined the flow within the droplet and the substrate in the CR, CA, SS, and SJ modes, where the evaporation problem is described in Section 2.6 and the imbibition problem is described by a local imbibition mass flux which is spatially uniform. The general solutions for the flow within the droplet and the substrate encompass (but are not limited to) the imbibition problems described in Sections 2.7.2 and 2.7.3, respectively. We found that the flow within the droplet is the sum of the evaporation and imbibition contributions, with the evaporation contribution dominating at the contact line, and that the flow within the substrate is always downwards in the CR, CA, SS, and SJ modes. In the CR mode, similarly to Section 4.2, the flow is always outwards and downwards within the droplet. In the CA mode, in contrast to Section 4.2, the flow within the droplet is always inwards and downwards, while for simultaneous evaporation and imbibition there are regions of outward, inward, and zero flow within the droplet, with the flow always being outwards at the contact line, so long as $\mathcal{E} > 0$. In the SS mode the behaviour of the flow within the droplet and the substrate in the CR and CA phases is qualitatively similar to the behaviour in CR and CA modes, respectively, and in the SJ mode the behaviour of the flow within the droplet and the substrate in the n th CR phase is qualitatively similar to the CR mode.

The results described in Chapter 4 indicate that the evaporation contribution to the mean flow dominates at the contact line on anisotropic porous substrates. However, since in reality evaporation cannot ever be completely turned off, experimentalists working with flooded, isotropic, porous substrates may struggle to distinguish whether evaporation or imbibition is responsible for the increased mean flow at the contact line. This ambiguity does not arise on an anisotropic porous substrate. We note that the flow within the droplet and the substrate could be visualised using the methods discussed in Sections 1.2 and 1.3, respectively, providing experimental routes to verify and validate the analytical expressions determined within Chapter 4. Moreover, the finding that a spatially uniform local imbibition mass flux produces inwards flow within

Chapter 4. Flow Within the Droplet and the Substrate

the droplet in the CA mode provides a testable prediction, and offers another layer of model verification and validation, on top of the standard comparison for the evolution of the droplet via R and/or θ , as discussed in Chapter 3. Having determined the flow within the droplet and the substrate, in Chapter 5 we consider the implications that the flow dynamics have on the transport and deposition of particles within a thin, particle-laden, sessile droplet.

Chapter 5

Transport and Deposition of Particles

5.1 Overview

In this chapter, we determine the transport, and deposition onto the substrate, of the particles within a droplet undergoing simultaneous evaporation and imbibition in the CR, CA, SS, and SJ modes, as formulated in Section 2.8, under the crucial condition that $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$. In Section 5.2 we determine the transport, and deposition onto the substrate, of the particles on an infinitely thick, isotropic, flooded, porous substrate, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.1, respectively. In Section 5.3 we determine the transport, and deposition onto the substrate, of the particles on a finitely thick, anisotropic, dry or flooded, porous substrate, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.1 or 2.7.2, respectively.

Substituting $\hat{U}_{\text{ref}} = \hat{U}_{\text{E,ref}}$ given by equations (2.25) into (2.68) shows that

$$\text{Pe}^* = \frac{\hat{\theta}_0 \hat{D}(\hat{c}_{\text{sat}} - c_\infty)}{\hat{\rho} \hat{D}_{\text{p}}} \quad (5.1)$$

for situations in which evaporation dominates, while substituting $\hat{U}_{\text{ref}} = \hat{U}_{\text{I,ref}}$ given by

equations (2.35), (2.48), and (2.60), respectively, into (2.68) shows that

$$\text{Pe}^* = \frac{\hat{\theta}_0^2 \hat{\gamma} \hat{k}}{\hat{R}_0 \hat{\mu} \hat{D}_p}, \quad \text{Pe}^* = \frac{\varphi \hat{k} \hat{P}_c}{\hat{\mu} \hat{D}_p}, \quad \text{and} \quad \text{Pe}^* = \frac{\hat{\theta}_0^2 \hat{\gamma} \hat{k}}{\hat{\mu} \hat{d} \hat{D}_p} \quad (5.2)$$

for situations in which imbibition dominates on the three porous substrates described in Sections 2.7.1, 2.7.2, and 2.7.3, respectively.

5.2 An infinitely thick, isotropic, flooded, porous substrate

In this section, we describe the transport of, and deposition onto the substrate of, the particles. Specifically, we determine the evolution of the concentration of particles within the droplet, ϕ , and the mass of particles within the droplet, M_{drop} , and deposited onto the substrate, M_{ring} or M_{rings} and/or M_{dist} , and (where appropriate) the final density per unit area of the distributed deposit of particles on the substrate, ϕ_{dist} . Note that many of the expressions obtained in this section do not depend explicitly on $\mathcal{E}$ and $\mathcal{I}$ when they are written in terms of R and/or θ (although they do, of course, depend implicitly on both $\mathcal{E}$ and $\mathcal{I}$ when they are written in terms of t). As a consequence, although they differ when expressed as functions of t , a number of the expressions given below coincide with those recently obtained by D'Ambrosio *et al.* [84] in their work on the effect of contact-line motion on the deposition of particles from a droplet undergoing pure evaporation.

5.2.1 CR Mode

For a droplet evolving in the CR mode, the characteristic equations (2.78) may be expressed as

$$\frac{d\phi}{d\theta} = \frac{\phi (\mathcal{E} J_E + \mathcal{I} J_I)}{h \, d\theta/dt} \quad \text{and} \quad \frac{dr}{d\theta} = \frac{\bar{u}}{d\theta/dt}. \quad (5.3a,b)$$

Substituting the expressions for h , J_E , J_I , R , θ , and $\bar{u}$ given by equations (2.8), (2.32), (2.44), (3.4), and (4.2), respectively, into (5.3b) and solving for r_0 yields

$$r_0 = \left[1 - \theta^{1/2} \left\{ \theta^{-3/4} - 1 + (1 - r^2)^{3/2} \right\}^{2/3} \right]^{1/2}. \quad (5.4)$$

Setting $r = 1$ in (5.4) shows that the initial position of a particle that has travelled to the pinned contact line is given by

$$r_0(1, t) = \left[1 - \left(1 - \theta^{3/4} \right)^{2/3} \right]^{1/2}. \quad (5.5)$$

Substituting the expression for the evolution of θ in the CR mode given by (3.4) into (5.5) we find that the time for a particle that is at the initial position $r = r_0$ to reach the pinned contact line, denoted by $t = t_{\text{ring}} = t_{\text{ring}}(r_0)$, is given by

$$t_{\text{ring}} = \frac{\pi}{32\mathcal{I}} \log \left[\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E} + 2\mathcal{I} \left\{ 1 - (1 - r_0^2)^{3/2} \right\}^{4/3}} \right]. \quad (5.6)$$

In particular, for a droplet undergoing pure evaporation

$$t_{\text{ring}} = \frac{\pi}{16} \left[1 - \left\{ 1 - (1 - r_0^2)^{3/2} \right\}^{4/3} \right], \quad (5.7)$$

while for a droplet undergoing pure imbibition

$$t_{\text{ring}} = \frac{\pi}{32} \log \left[\left\{ 1 - (1 - r_0^2)^{3/2} \right\}^{-4/3} \right]. \quad (5.8)$$

Figure 5.1(a) shows $t_{\text{ring}}/t_{\text{CR}}$ plotted as a function of r_0 for a range of values of $\mathcal{I}$. In particular, Figure 5.1(a) shows that t_{ring} decreases monotonically from $t_{\text{ring}} = t_{\text{CR}}$ at $r_0 = 0$ to $t_{\text{ring}} = 0$ at $r_0 = 1$, i.e., particles that are initially near the contact line are deposited (in the ring deposit) before those that are initially near the centre of the droplet.

Substituting the expression for r given implicitly by (5.4) into (5.3b) and solving

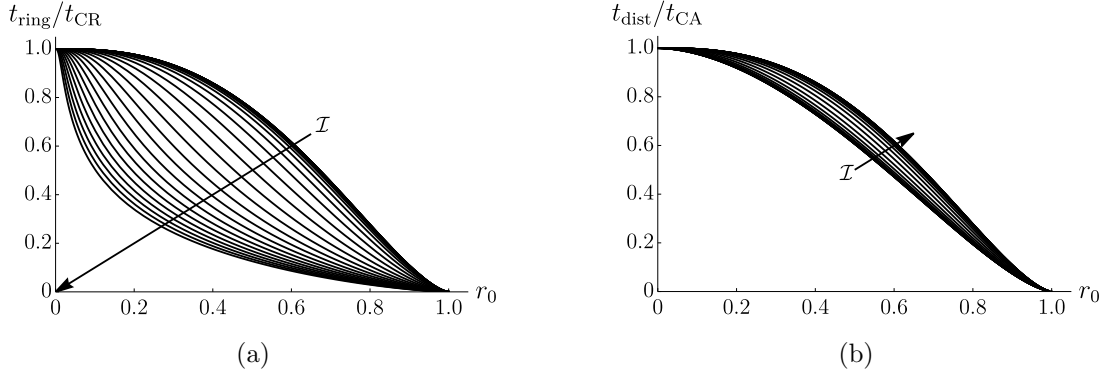


Figure 5.1: (a) $t_{\text{ring}}/t_{\text{CR}}$ given by (5.6) and (b) $t_{\text{dist}}/t_{\text{CA}}$ given by (5.18) plotted as functions of r_0 for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$). The arrows indicate the directions of increasing $\mathcal{I}$.

for ϕ shows that

$$\phi = \left[1 + \left(\theta^{3/4} - 1 \right) (1 - r_0^2)^{-3/2} \right]^{-1/3}. \quad (5.9)$$

Using (5.4) to eliminate r_0 yields

$$\phi = \left[1 + \left(\theta^{-3/4} - 1 \right) (1 - r^2)^{-3/2} \right]^{1/3}, \quad (5.10)$$

and hence

$$\phi h = \frac{\theta (1 - r^2)}{2} \left[1 + \left(\theta^{-3/4} - 1 \right) (1 - r^2)^{-3/2} \right]^{1/3} \quad (5.11)$$

(see, for example, Zheng [65] and D'Ambrosio *et al.* [82]). Figure 5.2 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of θ . In particular, Figure 5.2(a) illustrates that ϕ is a monotonically increasing function of r that takes its minimum value at the centre of the droplet according to $\phi = O(1) = \theta^{-1/4}$ as $r \rightarrow 0^+$ and is singular at the contact line according to $\phi = O((1 - r)^{-1/2}) \rightarrow \infty$ as $r \rightarrow 1^-$, and a monotonically decreasing function of θ (i.e., a monotonically increasing function of t). On the other hand, Figure 5.2(b) illustrates that ϕh is a monotonically decreasing function of r that takes its maximum value at the centre of the droplet according to $\phi h = O(1) = \theta^{3/4}/2$ as $r \rightarrow 0^+$ and goes to zero at the contact line according to $\phi h = O((1 - r)^{1/2}) \rightarrow 0^+$ as $r \rightarrow 1^-$, and is a monotonically increasing function of θ (i.e., a monotonically decreasing function of t) near the centre of the droplet but a

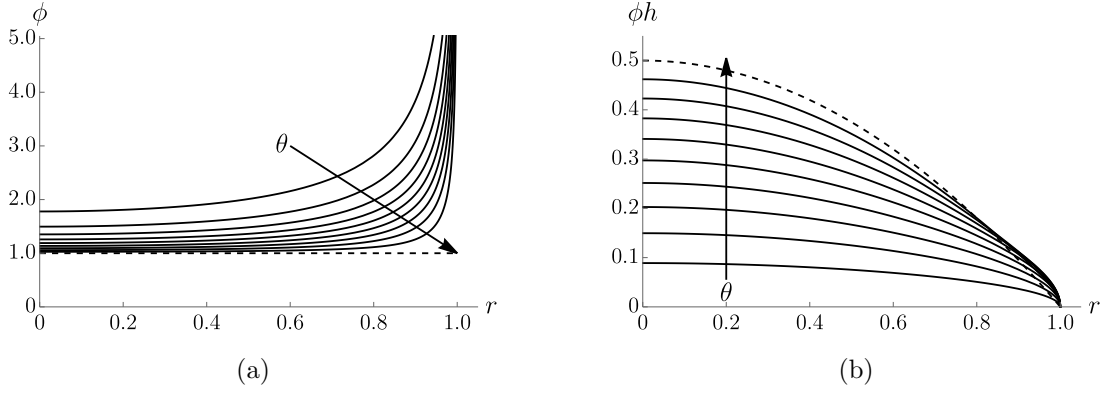


Figure 5.2: (a) ϕ given by (5.10) and (b) ϕh given by (5.11) in the CR mode plotted as functions of r for $\theta = 1/10, 1/5, \dots, 9/10$. The dashed lines indicate the initial values $\phi_0(r) \equiv 1$ and $\phi_0(r)h(r, 0) = (1 - r^2)/2$ corresponding to $\theta = 1$, and the arrows indicate the directions of increasing θ .

non-monotonic function of θ (i.e., a non-monotonic function of t) near the contact line. In particular, $\phi h \rightarrow 0^+$ everywhere within the droplet as $\theta \rightarrow 0^+$ (i.e., as $t \rightarrow t_{\text{CR}}^-$), showing that all of the particles eventually leave the droplet, and in this mode are eventually transferred to the ring deposit at $r = 1$ (i.e., at the pinned contact line).

Substituting the expression for $r_0(1, t)$ given by (5.5) into (2.80) and (2.84) shows that M_{drop} and M_{ring} are given by

$$M_{\text{drop}} = M_0 \left[1 - \left(1 - \theta^{3/4} \right)^{4/3} \right] \quad (5.12)$$

and

$$M_{\text{ring}} = M_0 \left(1 - \theta^{3/4} \right)^{4/3}, \quad (5.13)$$

respectively (see, for example, Deegan *et al.* [53], Boulogne *et al.* [79], and D'Ambrosio *et al.* [82]), together with $M_{\text{dist}} \equiv 0$. Figure 5.3(a) shows the evolutions of M_{drop}/M_0 and M_{ring}/M_0 plotted as functions of t/t_{CR} for a range of values of $\mathcal{I}$. In particular, Figure 5.3(a) illustrates how, as in the extensively studied situation of a droplet undergoing pure evaporation in the CR mode, all of the particles initially within the droplet are eventually transferred to the ring deposit at $r = 1$.

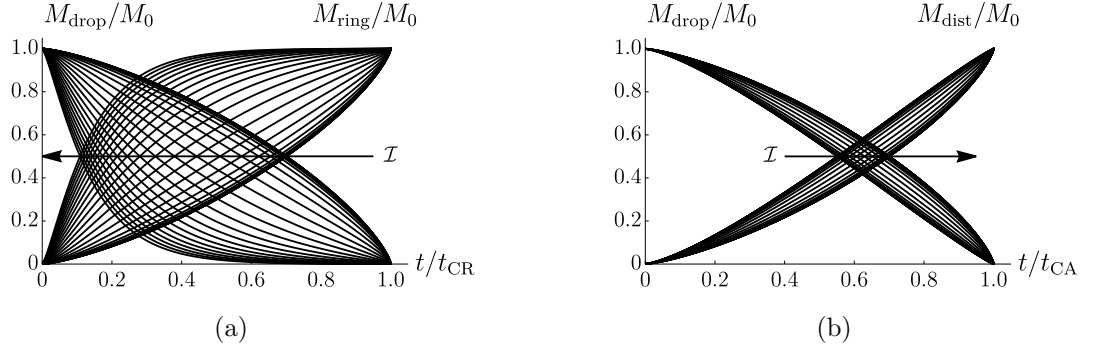


Figure 5.3: The evolutions of (a) M_{drop}/M_0 and M_{ring}/M_0 plotted as functions of t/t_{CR} in the CR mode and (b) M_{drop}/M_0 and M_{dist}/M_0 plotted as functions of t/t_{CA} in the CA mode for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$). The arrows indicate the directions of increasing $\mathcal{I}$.

5.2.2 CA Mode

For a droplet evolving in the CA mode, the characteristic equations (2.78) may be expressed as

$$\frac{d\phi}{dR} = \frac{\phi(\mathcal{E}J_E + \mathcal{I}J_I)}{h \, dR/dt} \quad \text{and} \quad \frac{dr}{dR} = \frac{\bar{u}}{dR/dt}. \quad (5.14\text{a,b})$$

Substituting the expressions for h , J_E , J_I , R , θ , and $\bar{u}$ given by equations (2.8), (2.32), (2.44), (3.9), and (4.17), respectively, into (5.14b) and solving for r_0 yields

$$r_0 = \left[1 - R^{3/2} \left\{ R^{-9/4} - 1 + \left(1 - \frac{r^2}{R^2} \right)^{3/2} \right\}^{2/3} \right]^{1/2}. \quad (5.15)$$

Setting $r = R$ in (5.15) shows that the initial position of a particle that has travelled to the unpinned contact line is given by

$$r_0(R, t) = \left[1 - \left(1 - R^{9/4} \right)^{2/3} \right]^{1/2}. \quad (5.16)$$

The expression for the evolution of R in the CA mode given by (3.9) is implicit, but an explicit expression for the time for a particle that is at the initial position $r = r_0$ to reach the unpinned contact line, denoted by $t = t_{\text{dist}} = t_{\text{dist}}(r_0)$, can be obtained by

rearranging (5.16) for R in terms of r_0 to yield

$$R = \left[1 - (1 - r_0^2)^{3/2} \right]^{4/9} \quad (5.17)$$

and substituting (5.17) into (3.9) to yield t_{dist} given by

$$t_{\text{dist}} = \frac{3\pi}{32\mathcal{E}^3} \left[8\mathcal{I}^2 \log \left(\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E} \left[1 - (1 - r_0^2)^{3/2} \right]^{4/9} + 2\mathcal{I}} \right) + \mathcal{E} \left(1 - \left[1 - (1 - r_0^2)^{3/2} \right]^{4/9} \right) \{ \mathcal{E} \left(\left[1 - (1 - r_0^2)^{3/2} \right]^{4/9} + 1 \right) - 4\mathcal{I} \} \right]. \quad (5.18)$$

In particular, for a droplet undergoing pure evaporation

$$t_{\text{dist}} = \frac{3\pi}{32} \left[1 - \left(1 - (1 - r_0^2)^{3/2} \right)^{8/9} \right], \quad (5.19)$$

while for a droplet undergoing pure imbibition

$$t_{\text{dist}} = \frac{\pi}{32} \left[1 - \left(1 - (1 - r_0^2)^{3/2} \right)^{4/3} \right]. \quad (5.20)$$

Figure 5.1(b) shows $t_{\text{dist}}/t_{\text{CA}}$ plotted as a function of r_0 for a range of values of $\mathcal{I}$. In particular, Figure 5.1(b) shows that t_{dist} decreases monotonically from $t_{\text{dist}} = t_{\text{CA}}$ at $r_0 = 0$ to $t_{\text{dist}} = 0$ at $r_0 = 1$, i.e., particles that are initially near the contact line are deposited (in the distributed deposit) before those that are initially near the centre of the droplet.

Substituting the expression for r given implicitly by (5.15) into (5.14a) and solving for ϕ shows that

$$\phi = \left[1 + \left(R^{9/4} - 1 \right) \left(1 - r_0^2 \right)^{-3/2} \right]^{-1/3}. \quad (5.21)$$

Using (5.15) to eliminate r_0 yields

$$\phi = \left[1 + \left(R^{9/4} - 1 \right) \left(1 - \frac{r^2}{R^2} \right)^{-3/2} \right]^{1/3}, \quad (5.22)$$

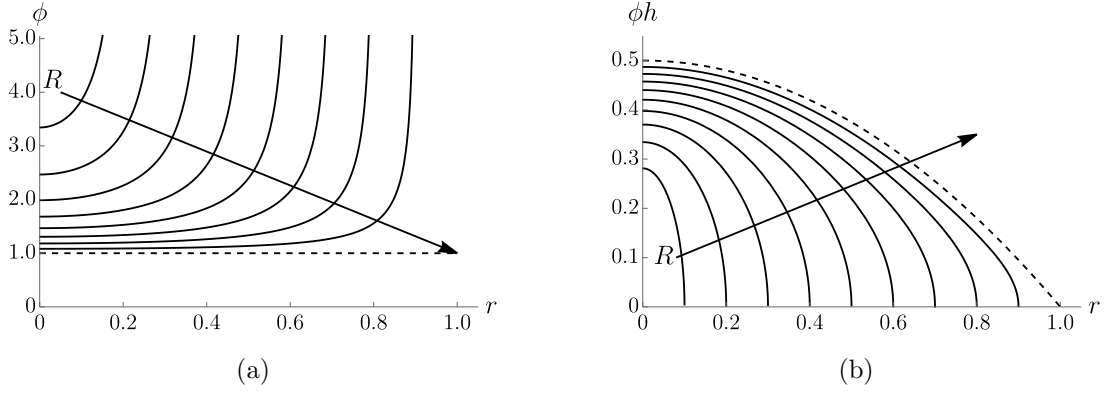


Figure 5.4: (a) ϕ given by (5.22) and (b) ϕh given by (5.23) in the CA mode plotted as functions of r for $R = 1/10, 1/5, \dots, 9/10$. The dashed lines indicate the initial values $\phi_0(r) \equiv 1$ and $\phi_0(r)h(r, 0) = (1 - r^2)/2$ corresponding to $R = 1$, and the arrows indicate the directions of increasing R .

and hence

$$\phi h = \frac{R}{2} \left(1 - \frac{r^2}{R^2}\right) \left[1 + \left(R^{-9/4} - 1\right) \left(1 - \frac{r^2}{R^2}\right)^{-3/2}\right]^{1/3}. \quad (5.23)$$

Figure 5.4 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of R . In particular, Figure 5.4(a) illustrates that ϕ is a monotonically increasing function of r that takes its minimum value at the centre of the droplet according to $\phi = O(1) = R^{-3/4}$ as $r \rightarrow 0^+$ and is singular at the contact line according to $\phi = O((R - r)^{-1/2})$ as $r \rightarrow R^-$, and a monotonically decreasing function of R (i.e., a monotonically increasing function of t). On the other hand, Figure 5.4(b) illustrates that ϕh is a monotonically decreasing function of r that takes its maximum value at the centre of the droplet according to $\phi h = O(1) = R^{1/4}/2$ as $r \rightarrow 0^+$ and goes to zero at the contact line according to $\phi h = O((R - r)^{1/2}) \rightarrow 0^+$ as $r \rightarrow R^-$, and is a monotonically increasing function of R (i.e., a monotonically decreasing function of t). In particular, $\phi h \rightarrow 0^+$ everywhere within the droplet as $R \rightarrow 0^+$, i.e., as $t \rightarrow t_{CA}^-$, showing that all of the particles eventually leave the droplet, and in this mode are eventually transferred to the distributed deposit in $0 \leq r < 1$.

Substituting the expression for $r_0(R, t)$ given by (5.16) into (2.80) and (2.87) shows

that M_{drop} and M_{dist} are given by

$$M_{\text{drop}} = M_0 \left[1 - \left(1 - R^{9/4} \right)^{4/3} \right] \quad (5.24)$$

and

$$M_{\text{dist}} = M_0 \left(1 - R^{9/4} \right)^{4/3}, \quad (5.25)$$

respectively, together with $M_{\text{ring}} \equiv 0$. Figure 5.3(b) shows the evolutions of M_{drop}/M_0 and M_{dist}/M_0 plotted as functions of t/t_{CA} for a range of values of $\mathcal{I}$. In particular, Figure 5.3(b) illustrates how, as in the situation of a droplet undergoing pure evaporation in the CA mode studied by D'Ambrosio *et al.* [84], all of the particles initially within the droplet are eventually transferred to the distributed deposit in $0 \leq r < 1$.

Substituting the expressions for h , r_0 , and ϕ given by equations (2.8), (5.15), and (5.22), respectively, into (2.88) shows that the final density per unit area of the distributed deposit of particles on the substrate, ϕ_{dist} , is given by

$$\phi_{\text{dist}} = \frac{3r^{1/4}}{8} \left(1 - r^{9/4} \right)^{1/3} \quad (5.26)$$

(see D'Ambrosio *et al.* [84]), i.e., the final density of the distributed deposit in the CA mode is zero at both the centre of the droplet and at the initial position of the contact line, and takes its maximum value of $\phi_{\text{dist}} = 3^{4/3} 2^{-35/9} \simeq 0.2921$ at $r = 2^{-8/9} \simeq 0.5400$. Note that, perhaps rather unexpectedly, the final density of the distributed deposit ϕ_{dist} (but not, of course, the temporal evolution towards it) is independent of the values of $\mathcal{E}$ and $\mathcal{I}$, i.e., is independent of both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet. We find that for a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate in the CA mode the nature of the final deposit is near-uniform, as sketched in Figure 1.7(e).

5.2.3 SS Mode

For a droplet evolving in the SS mode, the characteristic equations are given by (5.3) in the CR phase for $0 \leq t \leq t^*$ and (5.14) in the CA phase for $t^* < t \leq t_{\text{SS}}$. Hence the solution for r_0 is given by (5.4) in the CR phase and (5.15) in the CA phase, and the corresponding expressions for t_{ring} and t_{dist} can be calculated in the same way as described previously for the CR and CA modes, respectively. The solution for t_{ring} in the CR phase is given by (5.6) for $0 \leq t \leq t^*$ and t_{dist} in the CA phase is given by

$$\begin{aligned}
t_{\text{dist}} = & \frac{3\pi\theta^*}{32\mathcal{E}^3} \left[8\mathcal{I}^2\theta^{*2} \log \left(\frac{\mathcal{E} + 2\mathcal{I}\theta^*}{\mathcal{E} [1 - (1 - r_0^2)^{3/2}]^{4/9} + 2\mathcal{I}\theta^*} \right) \right. \\
& + \mathcal{E} \left(1 - [1 - (1 - r_0^2)^{3/2}]^{4/9} \right) \left\{ \mathcal{E} \left([1 - (1 - r_0^2)^{3/2}]^{4/9} + 1 \right) - 4\mathcal{I}\theta^* \right\} \Big] \\
& + \frac{\pi}{32\mathcal{I}} \log \left(\frac{\mathcal{E} + 2\mathcal{I}}{\mathcal{E} + 2\mathcal{I}\theta^*} \right)
\end{aligned} \tag{5.27}$$

for $t^* < t \leq t_{\text{SS}}$. In particular, for a droplet undergoing pure evaporation t_{dist} in the CA phase is given by

$$t_{\text{dist}} = \frac{3\pi\theta^*}{32} \left(1 - [1 - (1 - r_0^2)^{3/2}]^{8/9} \right) + \frac{\pi(1 - \theta^*)}{16} \tag{5.28}$$

for $t^* < t \leq t_{\text{SS}}$, while for a droplet undergoing pure imbibition t_{dist} in the CA phase is given by

$$t_{\text{dist}} = \frac{\pi}{32} \left(1 - [1 - (1 - r_0^2)^{3/2}]^{4/3} \right) - \frac{\pi}{32} \log \theta^* \tag{5.29}$$

for $t^* < t \leq t_{\text{SS}}$. Figures 5.5, 5.6, and 5.7 show (a) $t_{\text{ring}}/t_{\text{SS}}$ and (b) $t_{\text{dist}}/t_{\text{SS}}$ plotted as functions of r_0 for a range of values of θ^* for a droplet undergoing pure evaporation, simultaneous evaporation and imbibition, and pure evaporation in the CR phase and CA phase of the SS mode, respectively. In particular, Figures 5.5, 5.6, and 5.7 illustrate that both quantities inherit their corresponding behaviours in the CR and CA modes in the corresponding phases.

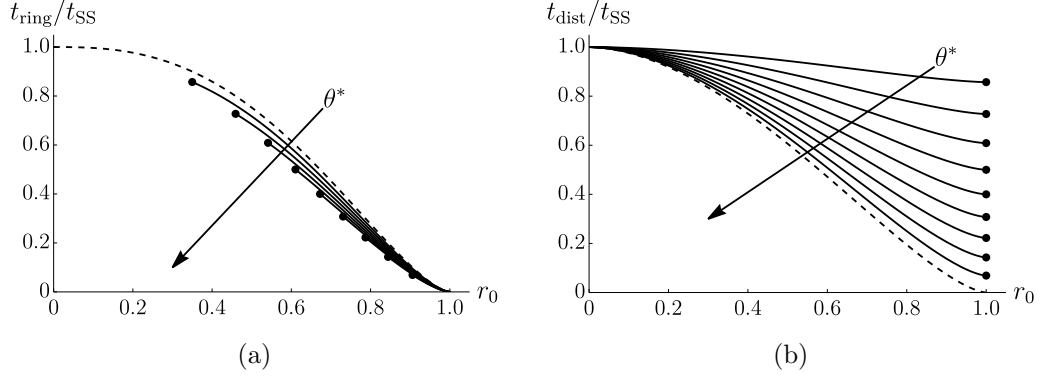


Figure 5.5: (a) $t_{\text{ring}}/t_{\text{SS}}$ given by (5.7) and (b) $t_{\text{dist}}/t_{\text{SS}}$ given by (5.28) plotted as functions of r_0 for a droplet undergoing pure evaporation, for $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed lines in (a,b) indicate the CR and CA mode solutions for $t_{\text{ring}}/t_{\text{CR}}$ and $t_{\text{dist}}/t_{\text{CA}}$, respectively. The arrows indicate the directions of increasing θ^* .

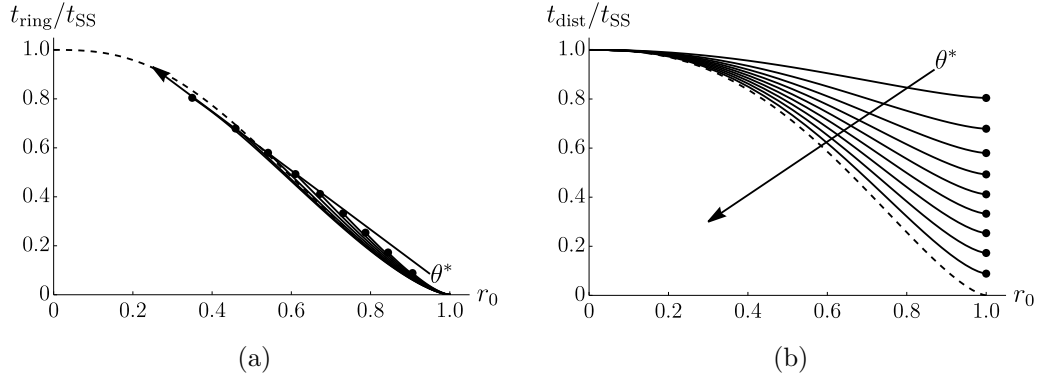


Figure 5.6: (a) $t_{\text{ring}}/t_{\text{SS}}$ given by (5.6) and (b) $t_{\text{dist}}/t_{\text{SS}}$ given by (5.27) plotted as functions of r_0 for a droplet undergoing simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) and $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed lines in (a,b) indicate the CR and CA mode solutions for $t_{\text{ring}}/t_{\text{CR}}$ and $t_{\text{dist}}/t_{\text{CA}}$, respectively. The arrows indicate the directions of increasing θ^* .

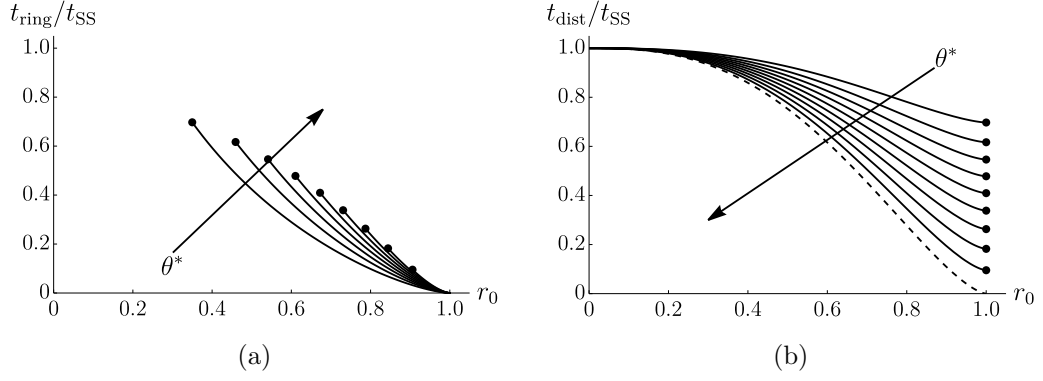


Figure 5.7: (a) $t_{\text{ring}}/t_{\text{SS}}$ given by (5.8) and (b) $t_{\text{dist}}/t_{\text{SS}}$ given by (5.29) plotted as functions of r_0 for a droplet undergoing pure imbibition, for $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed lines in (a,b) indicate the CR and CA mode solutions for $t_{\text{ring}}/t_{\text{CR}}$ and $t_{\text{dist}}/t_{\text{CA}}$, respectively. The arrows indicate the directions of increasing θ^* .

Solving for ϕ yields (5.10) in the CR phase and

$$\phi = \left[\frac{1 + (\theta^{*-3/4} - 1)(1 - r_0^2)^{-3/2}}{1 + (R^{9/4} - 1)(1 - r_0^2)^{-3/2}} \right]^{1/3} \quad (5.30)$$

in the CA phase. Hence ϕ is given by (5.10) in the CR phase and

$$\phi = \left[1 + (\theta^{*-3/4} R^{-9/4} - 1) \left(1 - \frac{r^2}{R^2} \right)^{-3/2} \right]^{1/3} \quad (5.31)$$

in the CA phase, and ϕh is given by (5.11) in the CR phase and

$$\phi h = \frac{\theta^* R}{2} \left(1 - \frac{r^2}{R^2} \right) \left[1 + (\theta^{*-3/4} R^{-9/4} - 1) \left(1 - \frac{r^2}{R^2} \right)^{-3/2} \right]^{1/3} \quad (5.32)$$

in the CA phase. Figure 5.8 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of θ in the CR phase and R in the CA phase. In particular, Figure 5.8 illustrates that both quantities inherit their corresponding behaviours in the CR and CA modes in the corresponding phases. In particular, $\phi h \rightarrow 0^+$ everywhere within the droplet as $R \rightarrow 0^+$, i.e., as $t \rightarrow t_{\text{SS}}^-$, showing that all of the particles eventually leave the droplet, and in this mode are eventually transferred to either the ring deposit at $r = 1$ or the distributed deposit in $0 \leq r < 1$.

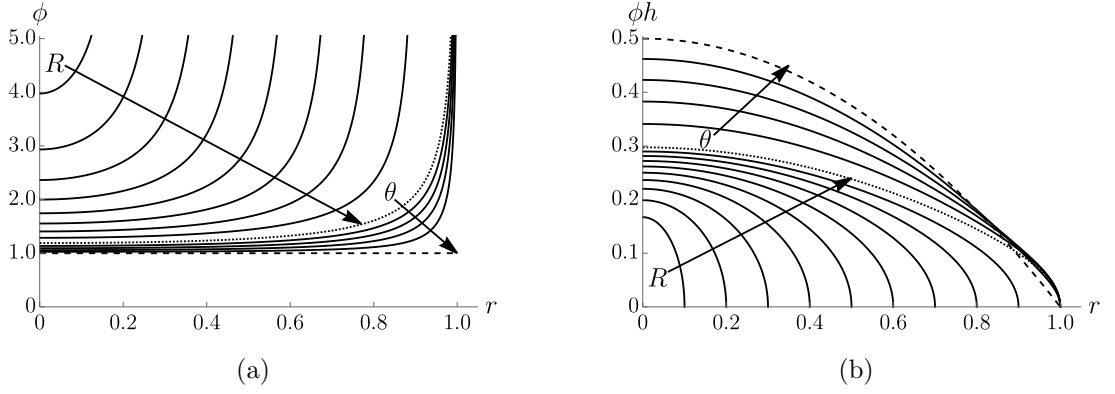


Figure 5.8: (a) ϕ given by (5.10) and (5.22) and (b) ϕh given by (5.11) and (5.23) in the SS mode plotted as functions of r for $\theta = 3/5, 7/10, 4/5, 9/10$ in the CR phase and $R = 1/10, 1/5, \dots, 9/10$ in the CA phase when $\theta^* = 1/2$. The dashed lines indicate the initial values $\phi_0(r) \equiv 1$ and $\phi_0(r)h(r,0) = (1-r^2)/2$ corresponding to $\theta = 1$, the dotted lines indicate the solution at $t = t^*$ corresponding to $\theta = \theta^* = 1/2$, and the arrows indicate the directions of increasing θ and R .

M_{drop} , M_{ring} and M_{dist} are given by (5.12), (5.13) and $M_{\text{dist}} \equiv 0$ in the CR phase, and by

$$M_{\text{drop}} = M_0 \left[1 - \left(1 - \theta^{*3/4} R^{9/4} \right)^{4/3} \right], \quad (5.33)$$

$$M_{\text{ring}} \equiv M_{\text{ring}}(t^*) = M_0 \left(1 - \theta^{*3/4} \right)^{4/3}, \quad (5.34)$$

and

$$M_{\text{dist}} = M_0 \left[\left(1 - \theta^{*3/4} R^{9/4} \right)^{4/3} - \left(1 - \theta^{*3/4} \right)^{4/3} \right] \quad (5.35)$$

in the CA phase. Figures 5.9(a,b,c) show the evolutions of (a) M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{dist}/M_0 plotted as functions of t/t_{SS} for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) when $\theta^* = 3/10$, while Figure 5.9(d) shows the final (scaled) masses in the deposit ring, $M_{\text{ring}}(t_{\text{SS}})/M_0 (= M_{\text{ring}}(t^*)/M_0)$, and in the distributed deposit, $M_{\text{dist}}(t_{\text{SS}})/M_0$, plotted as functions of θ^* . In particular, Figure 5.9(d) illustrates that there is a greater mass of particles in the final deposit ring than in the final distributed deposit (i.e., $M_{\text{ring}}(t_{\text{SS}}) > M_{\text{dist}}(t_{\text{SS}})$) when $0 \leq \theta^* < \theta_{\text{crit}}^*$, and vice versa (i.e., $M_{\text{ring}}(t_{\text{SS}}) < M_{\text{dist}}(t_{\text{SS}})$) for $\theta_{\text{crit}}^* < \theta^* \leq 1$, where $\theta_{\text{crit}}^* = (1 - 2^{-3/4})^{4/3} \simeq 0.3000$ is the critical value of θ^* for which $M_{\text{ring}}(t_{\text{SS}})/M_0 = M_{\text{dist}}(t_{\text{SS}})/M_0 = 1/2$.

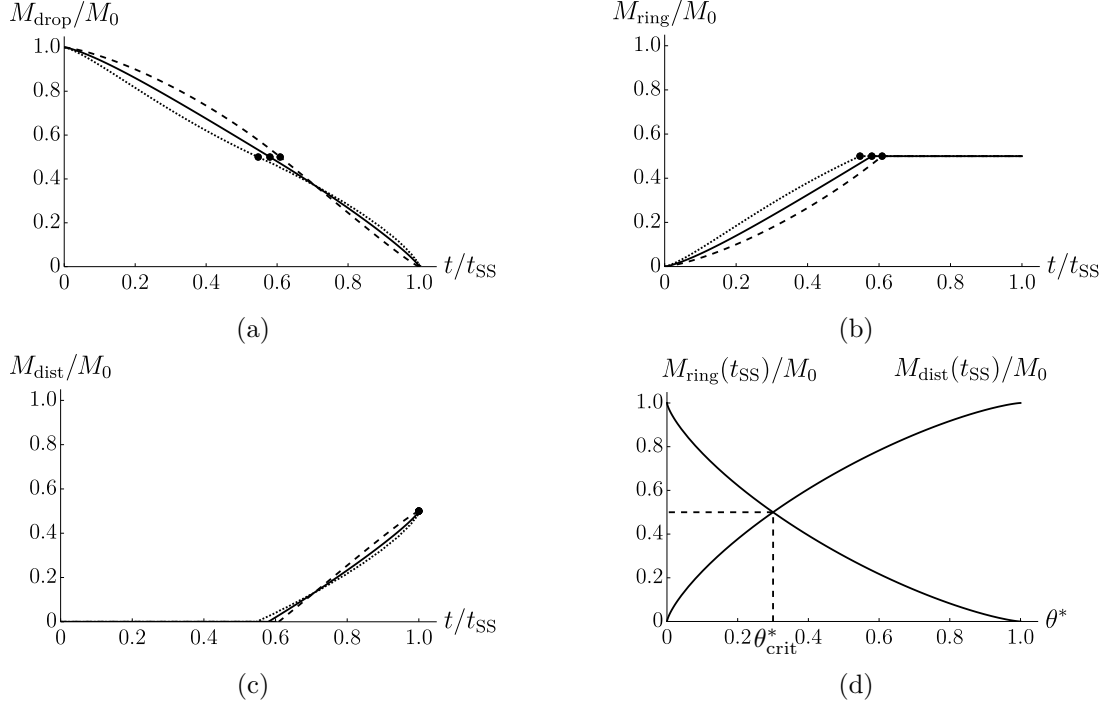


Figure 5.9: The evolutions of (a) M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{dist}/M_0 in the SS mode plotted as functions of t/t_{SS} for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) when $\theta^* = 3/10$. The dots in (a) denote the time at which the CR phase ends, i.e., $t = t^*$. (d) $M_{\text{ring}}(t_{\text{SS}})/M_0 (= M_{\text{ring}}(t^*)/M_0)$ and $M_{\text{dist}}(t_{\text{SS}})/M_0$ plotted as functions of θ^* in the SS mode. The dashed lines in (d) indicate the critical value of $\theta^* = \theta^*_{\text{crit}} = (1 - 2^{-3/4})^{4/3} \simeq 0.3000$ for which $M_{\text{ring}}(t_{\text{SS}})/M_0 = M_{\text{dist}}(t_{\text{SS}})/M_0 = 1/2$.

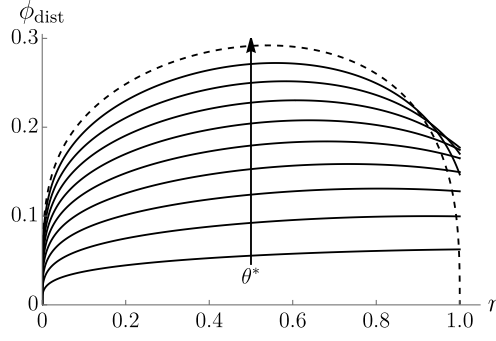


Figure 5.10: ϕ_{dist} given by (5.36) in the CA phase of the SS mode plotted as a function of r for $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed line indicates the solution in the CA mode given by (5.26) corresponding to $\theta^* = 1$, and the arrow indicates the directions of increasing θ^* .

Substituting the expressions for h , r_0 , and ϕ given by equations (2.8), (5.15), and (5.31), respectively, into (2.92) shows that in the CA phase of the SS mode ϕ_{dist} is given by

$$\phi_{\text{dist}} = \frac{3\theta^{*3/4}r^{1/4}}{8} \left(1 - \theta^{*3/4}r^{9/4}\right)^{1/3} \quad (5.36)$$

(see D'Ambrosio *et al.* [84]). Figure 5.10 shows ϕ_{dist} given by (5.36) plotted as a function of r for a range of values of θ^* , including the solution in the CA mode given by (5.26) corresponding to $\theta^* = 1$. In particular, Figure 5.10 illustrates that the final density of the distributed deposit in the SS mode is zero at the centre of the droplet, and takes its maximum value of $\phi_{\text{dist}} = 3\theta^{*3/4}(1 - \theta^{*3/4})^{1/3}/8$ at $r = 1$ (i.e., at the initial position of the contact line) for $0 < \theta^* \leq \theta_{\text{min}}^* = 2^{-8/3} \simeq 0.1575$ and $\phi_{\text{dist}} = 3^{4/3}2^{-35/9}\theta^{*2/3} \simeq 0.2921\theta^{*2/3}$ at $r = 2^{-8/9}\theta^{*-1/3} \simeq 0.5400\theta^{*-1/3}$ for $\theta_{\text{min}}^* < \theta^* \leq 1$. Note that, as in the CA mode and discussed in Section 5.2.2, a cleaved near-uniform deposit forms in the CA phase of the SS mode and the final density of the distributed deposit ϕ_{dist} is independent of the values of $\mathcal{E}$ and $\mathcal{I}$, i.e., is independent of both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet.

5.2.4 SJ Mode

For a droplet evolving in the SJ mode, the characteristic equations are given by (5.3) in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Hence the solution for $r_{0,n}$ is

$$r_{0,n} = R_n \left[1 - \left(\frac{\theta}{\theta_{\max}} \right)^{1/2} \left\{ \left(\frac{\theta}{\theta_{\max}} \right)^{-3/4} - 1 + \left(1 - \frac{r_0^2}{R_n^2} \right)^{3/2} \right\}^{2/3} \right]^{1/2} \quad (5.37)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Setting $r = R_n$ shows that

$$r_{0,n}(R_n, t) = R_n \left[1 - \left(\frac{\theta}{\theta_{\max}} \right)^{1/2} \left\{ \left(\frac{\theta}{\theta_{\max}} \right)^{-3/4} - 1 \right\}^{2/3} \right]^{1/2} \quad (5.38)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). The corresponding expression for the time for a particle that is at the initial position $r = r_{0,n}$ to reach the n th pinned contact line, denoted by $t = t_{\text{ring},n} = t_{\text{ring},n}(r_{0,n})$ can be calculated in the same way as described previously for t_{ring} in the CR mode (see D'Ambrosio *et al.* [84]), and is given by

$$t_{\text{ring},n} = t_{n-1} + \frac{\pi R_n^3}{32\mathcal{I}} \log \left(\frac{\mathcal{E} R_n + 2\mathcal{I}\theta_{\max}}{\mathcal{E} R_n + 2\mathcal{I}\theta_{\max} \left[1 - \left(1 - \frac{r_0^2}{R_n^2} \right)^{3/2} \right]^{4/3}} \right) \quad (5.39)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Note that, as discussed in Section 3.2, t_n must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition. In particular, for a droplet undergoing pure evaporation, $t_{\text{ring},n}$ is given by

$$\begin{aligned} t_{\text{ring},n} = & \frac{\pi(\theta_{\max} - \theta_{\min}) \left(1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2(n-1)/3} \right)}{16 \left(1 - \left(\frac{\theta_{\min}}{\theta_{\max}} \right)^{2/3} \right)} \\ & + \frac{\pi R_n^2 \theta_{\max}}{16} \left(1 - \left[1 - \left(1 - \frac{r_{0,n}^2}{R_n^2} \right)^{3/2} \right]^{4/3} \right) \end{aligned} \quad (5.40)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while for a droplet undergoing pure imbibition, $t_{\text{ring},n,\text{I}}$ is given by

$$t_{\text{ring},n} = \frac{\pi \left(1 - \left(\frac{\theta_{\min}}{\theta_{\max}}\right)^{n-1}\right)}{32 \left(1 - \frac{\theta_{\min}}{\theta_{\max}}\right)} \log \left(\frac{\theta_{\max}}{\theta_{\min}}\right) + \frac{\pi R_n^3}{32} \log \left(\left[1 - \left(1 - \frac{r_{0,n}^2}{R_n^2}\right)^{3/2} \right]^{-4/3} \right) \quad (5.41)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Figure 5.11 shows $t_{\text{ring},n}/t_{\text{SJ}}$ plotted as functions of $r_{0,n}$ for a droplet undergoing (a) pure evaporation, (b) simultaneous evaporation and imbibition, and (c) pure evaporation in each CR phase when $\theta_{\min} = 1/2$. In particular, Figure 5.11 illustrates that $t_{\text{ring},n}$ inherits the corresponding behaviour in the CR mode in each CR phase, i.e., particles that are initially near the n th contact line are deposited (in the n th ring deposit) before those that are initially near the centre of the droplet.

Solving for ϕ in the n th CR phase yields

$$\phi = \phi_{n,\max}(r_{0,n}) \left[1 + \left\{ \left(\frac{\theta}{\theta_{\max}}\right)^{3/4} - 1 \right\} \left(1 - \frac{r_{0,n}^2}{R_n^2}\right)^{-3/2} \right]^{-1/3} \quad (5.42)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), where $\phi_{n,\max}(r_{0,n}) = \phi(r_{0,n-1}, t_{n-1})$ denotes the concentration of particles within the droplet at the end of the $(n-1)$ th CR phase. Hence ϕ is given by

$$\phi = \left[1 + \left(\theta^{-3/4} R_n^{-9/4} - 1 \right) \left(1 - \frac{r^2}{R_n^2} \right)^{-3/2} \right]^{1/3} \quad (5.43)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) and ϕh is given by

$$\phi h = \frac{\theta R_n}{2} \left(1 - \frac{r^2}{R_n^2} \right) \left[1 + \left(\theta^{-3/4} R_n^{-9/4} - 1 \right) \left(1 - \frac{r^2}{R_n^2} \right)^{-3/2} \right]^{1/3} \quad (5.44)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Figure 5.12 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of θ in each CR phase. In particular, Figure 5.12 illustrates that both quantities inherit their corresponding behaviour in the CR mode

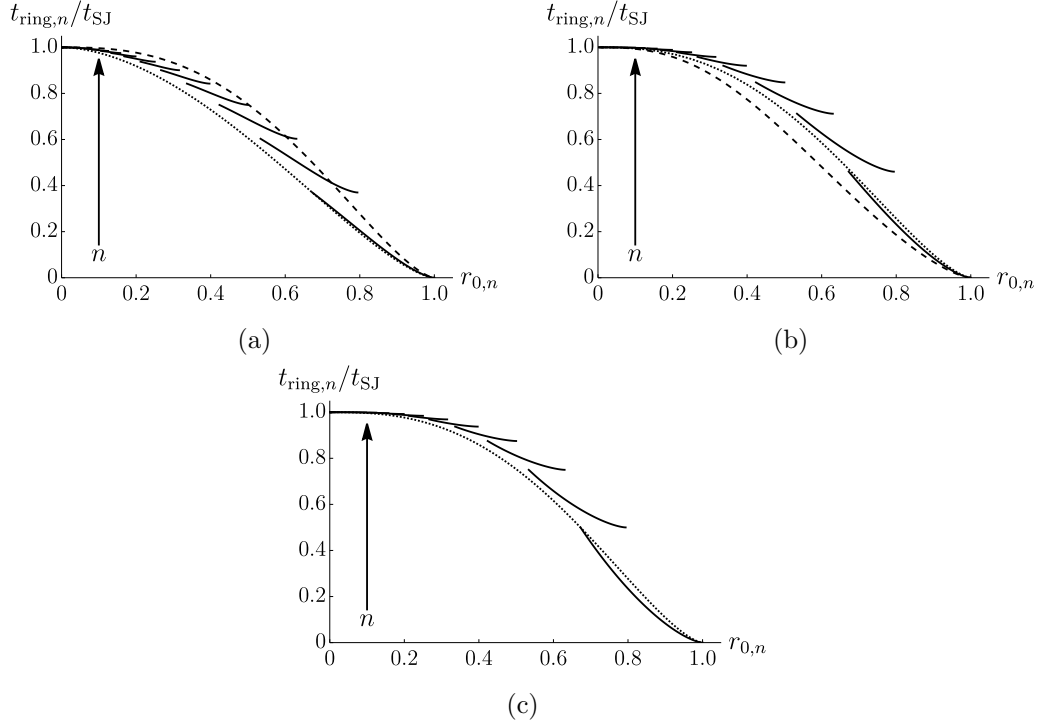


Figure 5.11: $t_{\text{ring},n}/t_{\text{SJ}}$ plotted as functions of $r_{0,n}$ in each CR phase for (a) pure evaporation, (b) simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$), and (c) pure imbibition when $\theta_{\min} = 1/2$. The dashed lines in (a,b) indicate the solutions for $t_{\text{ring}}/t_{\text{CR}}$ in the CR mode and the dotted lines in (a,b,c) indicate the solutions for $t_{\text{dist}}/t_{\text{CA}}$ in the CA mode, respectively. The arrows indicate the directions of increasing n .

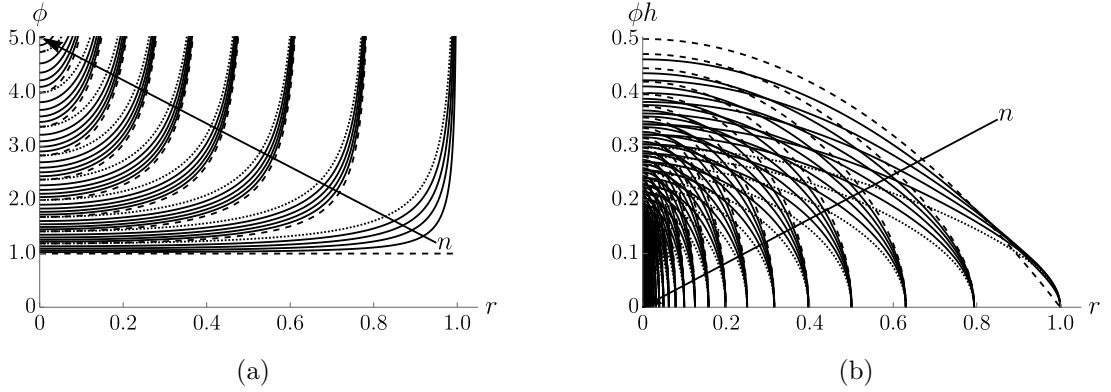


Figure 5.12: (a) ϕ given by (5.42) and (b) ϕh given by (5.44) in the SJ mode plotted as functions of r at $\theta = 3/5, 7/10, 4/5, 9/10$ in each CR phase when $\theta_{\min} = 1/2$. The dashed and the dotted lines indicate the values at $t = t_{n-1}$ and $t = t_n$ ($n = 1, 2, 3, \dots$) (i.e., at the start and the end of each CR phase) corresponding to $\theta = \theta_{\max} = 1$ and $\theta = \theta_{\min} = 1/2$, respectively, and the arrows indicate the directions of increasing n .

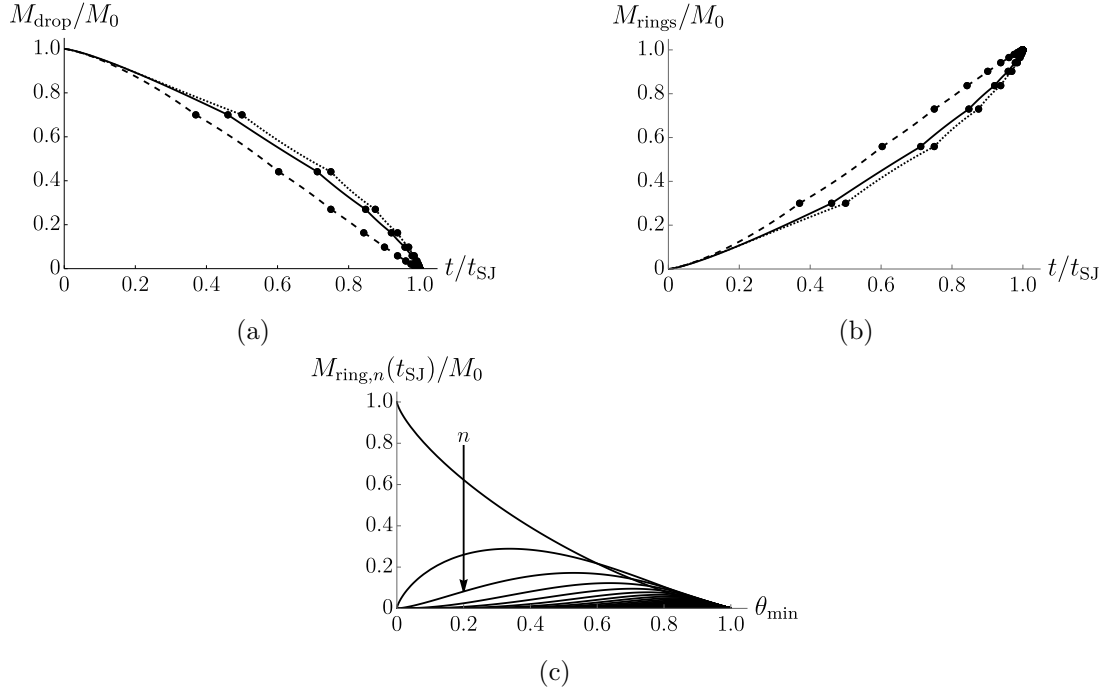


Figure 5.13: The evolutions of (a) M_{drop}/M_0 and (b) M_{rings}/M_0 in the SJ mode plotted as functions of t/t_{SJ} for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) when $\theta_{\text{min}} = 1/2$. The dots in (a) and (b) denote the times at which the n th CR phase ends, i.e., $t = t_n$ ($n = 1, 2, 3, \dots$). (c) $M_{\text{ring},n}(t_{\text{SJ}})/M_0 (= M_{\text{ring},n}(t_n)/M_0)$ in the SJ mode plotted as a function of θ_{min} for $n = 1, 2, 3, \dots$, and the arrow indicates the directions of increasing n .

in each CR phase. In particular, $\phi h \rightarrow 0^+$ everywhere within the droplet as $t \rightarrow t_{\text{SJ}}^-$, showing that all of the particles eventually leave the droplet, and in this mode are eventually transferred to the (theoretically infinite number of) ring deposits at $r = R_n$ ($n = 1, 2, 3, \dots$).

M_{drop} and $M_{\text{ring},n}$ are given by

$$M_{\text{drop}} = M_0 \left[1 - \left(1 - \theta^{3/4} R_n^{9/4} \right)^{4/3} \right] \quad (5.45)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) and

$$M_{\text{ring},n} = M_0 \left[\left(1 - \theta^{3/4} R_n^{9/4} \right)^{4/3} - \left(1 - \theta_{\text{max}}^{3/4} R_n^{9/4} \right)^{4/3} \right] \quad (5.46)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), together with M_{rings} , which is determined by summing the non-zero values of $M_{\text{ring},n}$, and $M_{\text{dist}} \equiv 0$. Figures 5.13(a,b) show the evolutions of (a) M_{drop}/M_0 and (b) M_{rings}/M_0 plotted as functions of t/t_{SJ} for pure evaporation (dashed line), simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$ (solid line), and pure imbibition (dotted line) when $\theta_{\text{min}} = 1/2$, while Figure 5.13(c) shows the final (scaled) mass of particles in the n th deposit ring, $M_{\text{ring},n}(t_{\text{SJ}})/M_0 (= M_{\text{ring},n}(t_n)/M_0)$, plotted as a function of θ_{min} for $n = 1, 2, 3, \dots$. In particular, Figure 5.13(c) illustrates that, as D'Ambrosio *et al.* [84] pointed out, $M_{\text{ring},n}(t_{\text{SJ}})$ decreases monotonically with n for $0 \leq \theta_{\text{min}} \leq \theta_{\text{min,crit}} = (2^{3/4} - 1)^{4/3} \simeq 0.6001$, but is non-monotonic for $\theta_{\text{min,crit}} \leq \theta_{\text{min}} \leq 1$.

5.3 Spatially Uniform Local Imbibition Mass Flux

In this section, we describe the transport of, and deposition onto the substrate of, the particles within a droplet undergoing imbibition on a porous substrate with a spatially uniform local imbibition mass flux. Specifically, we determine the evolution of the concentration of particles within the droplet, ϕ , and the mass of particles within the droplet, M_{drop} , and deposited onto the substrate, M_{ring} or M_{rings} and/or M_{dist} , and (where appropriate) the final density per unit area of the distributed deposit of particles on the substrate, ϕ_{dist} . Note that many of the expressions obtained in this section for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate also coincide with those for a droplet undergoing simultaneous evaporation and imbibition in situations where the evaporation is described by a spatially uniform local evaporative mass flux, when they are written in terms of R and/or θ (although they do, of course, depend implicitly on both $\mathcal{E}$ and $\mathcal{I}$ when written in terms of t). The evolution of ϕ , M_{drop} , M_{ring} and/or M_{rings} , M_{dist} , and ϕ_{dist} for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate must be evaluated numerically, which we implemented using Mathematica [238] routine `NDSolve[]`. Specifically, we used the automatic solver feature, which selects an appropriate numerical integration method

based on problem stiffness and structure, and confirmed convergence under refinement. We note that due to the computational expense we have chosen not to numerically evaluate ϕ , M_{drop} , M_{ring} and/or M_{rings} , M_{dist} , and ϕ_{dist} for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate in the SS and SJ modes. However, we carried out preliminary analysis which suggests that the behaviours are qualitatively similar to those in the CR and CA modes, as discussed in Sections 5.3.1 and 5.3.2, respectively.

5.3.1 CR Mode

Substituting h , J_E , J_I , R , θ , and $\bar{u}$ given by equations (2.8), (2.32), (2.57) or (2.65), (3.39) or (3.75), and (4.60), respectively, into (5.3b) we find that r_0 must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition in the CR mode. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate r_0 is given by

$$r_0 = r\theta^{1/4}. \quad (5.47)$$

Setting $r = 1$ in (5.47) shows that

$$r_0(1, t) = \theta^{1/4}. \quad (5.48)$$

We find that t_{ring} must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition. In particular, substituting the expression for the evolution of θ in the CR mode given by (3.41) into (5.48) we find that t_{ring} for a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate is given by

$$t_{\text{ring}} = \frac{(1 - r_0^4)^2}{32}, \quad (5.49)$$

while substituting the expression for the evolution of θ in the CR mode given by (3.77) into (5.48) we find that t_{ring} for a droplet undergoing pure imbibition on a finitely thick,

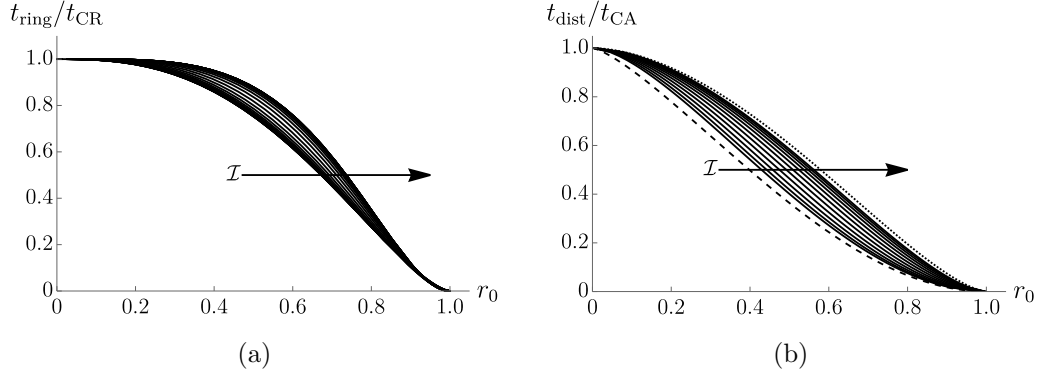


Figure 5.14: (a) $t_{\text{ring}}/t_{\text{CR}}$ and (b) $t_{\text{dist}}/t_{\text{CA}}$ plotted as functions of r_0 for pure evaporation (dashed lines), simultaneous evaporation and imbibition $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) (solid lines), and pure imbibition (dotted lines) on a finitely thick, anisotropic, initially dry, porous substrate. The arrows indicate the directions of increasing $\mathcal{I}$.

anisotropic, flooded, porous substrate is given by

$$t_{\text{ring}} = -\frac{1}{2} \log r_0. \quad (5.50)$$

Figures 5.14(a) and 5.15(a) show $t_{\text{ring}}/t_{\text{CR}}$ as a function of r_0 for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, dry and flooded, porous substrate, respectively. In particular, Figures 5.14(a) and 5.15(a) illustrate that the behaviour of t_{ring} for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate is qualitatively similar to the behaviour of t_{ring} given by (5.6), as discussed in Section 5.2.1, i.e., particles that are initially near the contact line are deposited (in the ring deposit) before those that are initially near the centre of the droplet.

We find that ϕ must also be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition in the CR mode, as discussed in Section 5.1. Substituting the expression for r given implicitly by (5.47) into (5.3a) and solving for ϕ shows that for a droplet undergoing pure imbibition on a finitely thick, anisotropic,

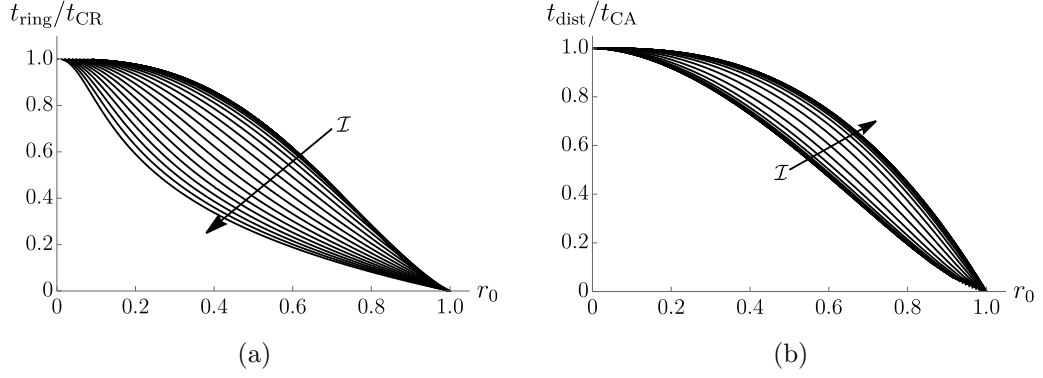


Figure 5.15: (a) $t_{\text{ring}}/t_{\text{CR}}$ and (b) $t_{\text{dist}}/t_{\text{CA}}$ plotted as functions of r_0 for simultaneous evaporation and imbibition $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) on a finitely thick, anisotropic, flooded, porous substrate. The arrows indicate the directions of increasing $\mathcal{I}$.

dry or flooded, porous substrate

$$\phi = \frac{1 - r_0^2}{\theta^{1/2} - r_0^2}. \quad (5.51)$$

Using (5.47) to eliminate r_0 yields

$$\phi = \frac{\theta^{-1/2} - r^2}{1 - r^2}, \quad (5.52)$$

and hence

$$\phi h = \frac{\theta(\theta^{-1/2} - r^2)}{2}. \quad (5.53)$$

We note that (5.53) is the same solution (when written in terms of θ) as that for a droplet undergoing pure evaporation according to a spatially uniform local evaporative mass flux, as discussed in Section 1.7 (see, for example, Zheng *et al.* [65], Zigelman & Manor [176], and D'Ambrosio *et al.* [82]). Figure 5.16 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of θ for pure evaporation (dashed lines), simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) (solid lines), and pure imbibition (dotted lines) on a finitely thick, anisotropic, initially dry, porous substrate. In particular, Figure 5.16(a) illustrates that ϕ is a monotonically increasing function of r that takes

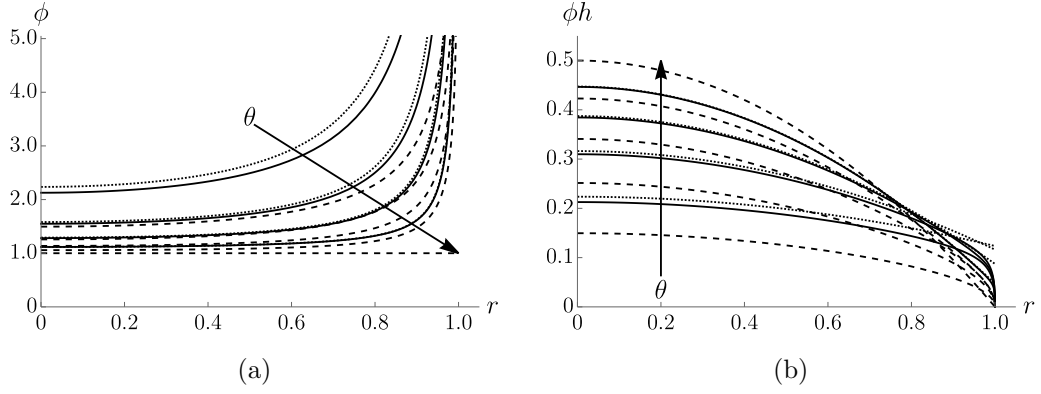


Figure 5.16: (a) ϕ and (b) ϕh in the CR mode plotted as functions of r for pure evaporation (dashed lines), simultaneous evaporation and imbibition (solid lines), and pure imbibition (dotted lines) on a finitely thick, anisotropic, initially dry, porous substrate, for $\theta = 1/5, 2/5, \dots, 4/5$. The dashed lines indicate the initial values $\phi_0(r) \equiv 1$ and $\phi_0(r)h(r, 0) = (1 - r^2)/2$ corresponding to $\theta = 1$, and the arrows indicate the directions of increasing θ .

its minimum value at the centre of the droplet and is singular at the contact line, and a monotonically decreasing function of θ (i.e., a monotonically increasing function of t). In particular, for a droplet undergoing pure evaporation we recover the behaviour of ϕ and ϕh discussed in Section 5.2.1, while for a droplet undergoing pure imbibition $\phi = O(1) = \theta^{-1/2}$ as $r \rightarrow 0^+$ and $\phi = O((1 - r)^{-1}) \rightarrow \infty$ as $r \rightarrow 1^-$ and, as one would expect, for a droplet undergoing simultaneous evaporation and imbibition the behaviour of ϕ at the centre and contact line of the droplet always lies between the two distinguished limits of a droplet undergoing pure evaporation or pure imbibition. Furthermore, Figure 5.16(b) illustrates that, in contrast to pure evaporation, for pure imbibition ϕh is a monotonically decreasing function of r that takes its maximum value at the centre of the droplet according to $\phi h = O(1) = \theta^{1/2}/2$ as $r \rightarrow 0^+$ and is non-zero at the contact line according to $\phi h = O(1) = (\theta/2)(\theta^{-1/2} - 1)$ as $r \rightarrow 1^-$, and is a monotonically increasing function of θ (i.e., a monotonically decreasing function of t) near the centre of the droplet but a non-monotonic function of θ (i.e., a non-monotonic function of t) near the contact line. We note that this behaviour is qualitatively similar for a droplet on a finitely thick, anisotropic, flooded, porous substrate, and hence, we have not plotted ϕ and ϕh in this situation.

Physically, the contrast between the pure evaporation and imbibition behaviour of ϕh at the contact line is due to the advection of particles towards the contact line being balanced by the mass flux of particles into the ring deposit for pure evaporation, whereas for pure imbibition the advection of particles towards the contact line exceeds the mass flux of particles into the ring deposit. Furthermore, Figure 5.16(b) illustrates that for simultaneous evaporation and imbibition ϕh is always zero at the contact line, as the evaporation contribution to advection always dominates as $r \rightarrow 1^-$, as discussed in Section 4.3.1, and hence so long as $\mathcal{E} > 0$ the advection of particles towards the contact line is balanced by the mass flux of particles transferred to the ring deposit. In particular, $\phi h \rightarrow 0^+$ everywhere within the droplet as $\theta \rightarrow 0^+$ (i.e., as $t \rightarrow t_{\text{CR}}^-$), showing that (similarly to Section 5.2.1) all of the particles eventually leave the droplet, and in this mode are eventually transferred to the ring deposit at $r = 1$ (i.e., at the pinned contact line).

We find that M_{drop} and M_{ring} must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition. Substituting the expression for $r_0(1, t)$ given by (5.48) into (2.80) and (2.84) shows that for a droplet undergoing pure imbibition M_{drop} and M_{ring} are given by

$$M_{\text{drop}} = M_0 \left(2\theta^{1/2} - \theta \right) \quad (5.54)$$

and

$$M_{\text{ring}} = M_0 \left[1 - \left(2\theta^{1/2} - \theta \right) \right], \quad (5.55)$$

respectively, together with $M_{\text{dist}} \equiv 0$ (see, for example, D'Ambrosio *et al.* [82] where (5.54) and (5.55) were given in the context of a droplet undergoing pure evaporation with a spatially uniform evaporative flux, as discussed in Section 1.7). Figures 5.17(a) and 5.18(a) shows the evolutions of M_{drop}/M_0 and M_{ring}/M_0 plotted as functions of t/t_{CR} for a range of values of $\mathcal{I}$ for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, dry and flooded, porous substrate, respectively. In particular, Figures 5.17(a) and 5.18(a) illustrate that, as discussed in Section

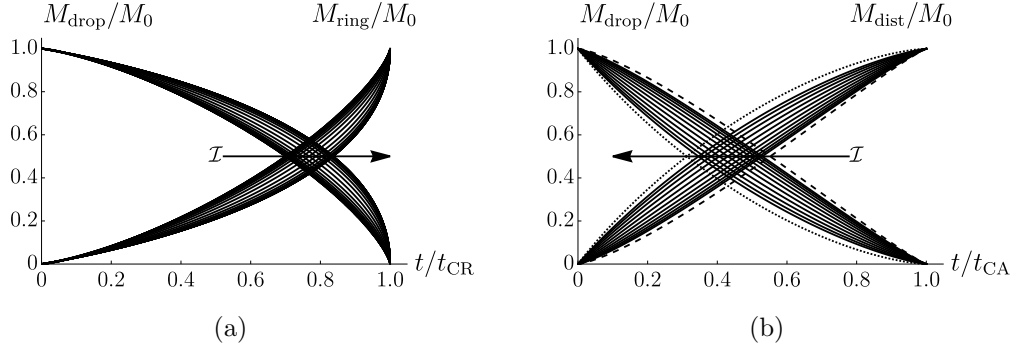


Figure 5.17: The evolutions of (a) M_{drop}/M_0 and M_{ring}/M_0 plotted as functions of t/t_{CR} in the CR mode and (b) M_{drop}/M_0 and M_{dist}/M_0 plotted as functions of t/t_{CA} in the CA mode for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -5, -4, \dots, 5$) for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, initially dry, porous substrate. The arrows indicate the directions of increasing $\mathcal{I}$.

5.2.1, all of the particles initially within the droplet are eventually transferred to the ring deposit at $r = 1$. Hence, the results presented in this section are in qualitative agreement with the experimental investigations of Dou & Derby [187] and Li *et al.* [6], as discussed in Section 1.7.

5.3.2 CA Mode

Substituting h , J_E , J_I , R , θ , and $\bar{u}$ given by equations (2.8), (2.32), (2.57) or (2.65), (3.43) or (3.78), and (4.75), respectively, into (5.14b) we find that r_0 must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition in the CA mode. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate r_0 is given by

$$r_0(r, t) = rR^{-1/4}. \quad (5.56)$$

Setting $r = R$ in (5.56) shows that

$$r_0(R, t) = R^{3/4}. \quad (5.57)$$

We find that t_{dist} must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition. In particular, substituting the expression for the

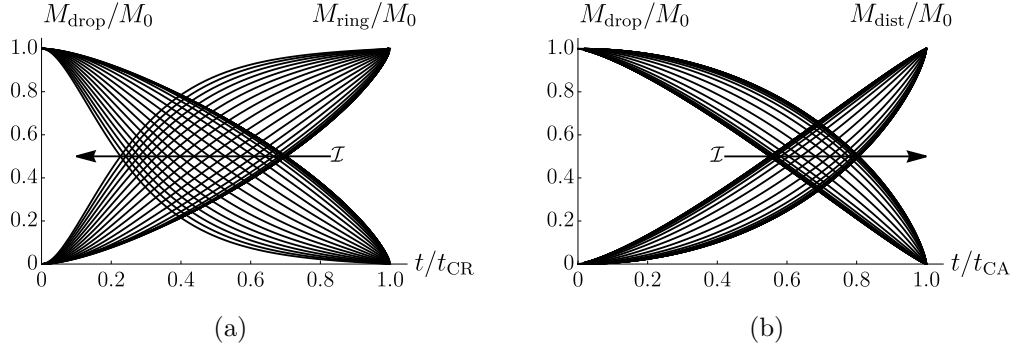


Figure 5.18: The evolutions of (a) M_{drop}/M_0 and M_{ring}/M_0 plotted as functions of t/t_{CR} in the CR mode and (b) M_{drop}/M_0 and M_{dist}/M_0 plotted as functions of t/t_{CA} in the CA mode for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$ ($n = -15, -14, \dots, 15$) for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, flooded, porous substrate. The arrows indicate the directions of increasing $\mathcal{I}$.

evolution of R in the CA mode given by (3.45) into (5.57) we find that t_{dist} for a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate is given by

$$t_{\text{dist}} = \frac{(1 - r_0^{4/3})^2}{32}, \quad (5.58)$$

while substituting the expression for the evolution of R in the CA mode given by (3.45) into (5.57) we find that t_{dist} for a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate is given by

$$t_{\text{dist}} = \frac{3(1 - r_0^{8/3})}{16}. \quad (5.59)$$

Figures 5.14(b) and 5.15(b) show $t_{\text{dist}}/t_{\text{CA}}$ plotted as functions of r_0 . In particular, Figures 5.14(b) and 5.15(b) illustrate that the behaviour of t_{dist} for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate is qualitatively similar to the behaviour of t_{dist} given by (5.18), i.e., particles that are initially near the contact line are deposited (in the distributed deposit) before those that are initially near the centre of the droplet, as discussed in Section 5.2.2.

We find that ϕ must also be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition in the CA mode. Substituting the expression for r given implicitly by (5.56) into (5.14b) and solving for ϕ shows that for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate

$$\phi = \frac{1 - r_0^2}{R^{3/2} - r_0^2}. \quad (5.60)$$

Using (5.56) to eliminate r_0 yields

$$\phi = \frac{R^{-3/2} - \frac{r^2}{R^2}}{1 - \frac{r^2}{R^2}}, \quad (5.61)$$

and hence

$$\phi h = \frac{R}{2} \left(R^{-3/2} - \frac{r^2}{R^2} \right). \quad (5.62)$$

We note that this is the same solution, when written in terms of R as for a droplet undergoing evaporation according to a spatially uniform local evaporative mass flux (see, for example, D'Ambrosio *et al.* [84]). Figure 5.19 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of R for pure evaporation (dashed lines), simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) (solid lines), and pure imbibition (dotted lines) for a droplet on a finitely thick, anisotropic, initially dry, porous substrate. In particular, Figure 5.19(a), illustrates that ϕ is a monotonically increasing function of r that takes its minimum value at the centre of the droplet and is singular at the contact line, and a monotonically decreasing function of R (i.e., a monotonically increasing function of t). In particular, for a droplet undergoing pure evaporation we recover the behaviour of ϕ and ϕh as discussed in Section 5.2.2, while for a droplet undergoing pure imbibition $\phi = O(1) = R^{-3/2}$ as $r \rightarrow 0^+$ and $\phi = O((R - r)^{-1}) \rightarrow \infty$ as $r \rightarrow R^-$ and, as one would expect, for a droplet undergoing simultaneous evaporation and imbibition the behaviour of ϕ at the centre and contact line of the droplet always lies between the two distinguished limits of a droplet undergoing pure evaporation or pure imbibition. Furthermore, Figure 5.19(b) illustrates that, in contrast to pure evaporation, for pure

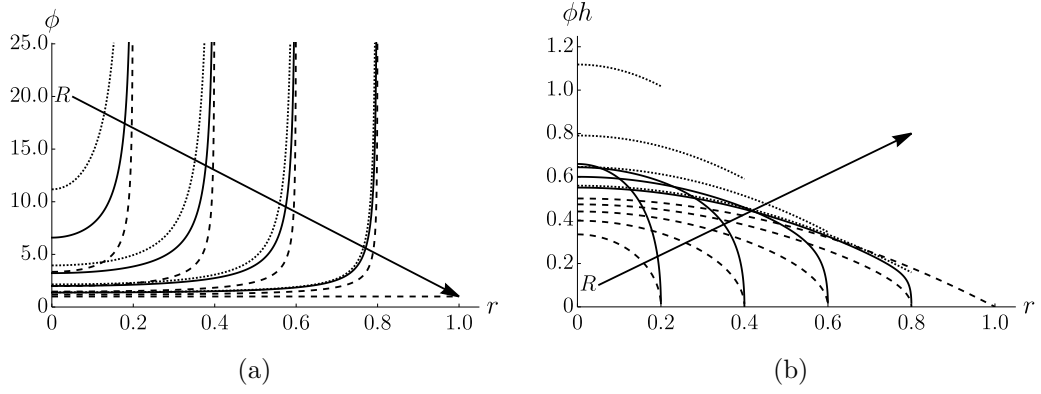


Figure 5.19: (a) ϕ and (b) ϕh in the CA mode plotted as functions of r for pure evaporation (dashed lines), simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) (solid lines), and pure imbibition (dotted lines) on a finitely thick, anisotropic, initially dry, porous substrate, for $R = 1/5, 2/5, \dots, 4/5$. The dashed lines indicate the initial values $\phi_0(r) \equiv 1$ and $\phi_0(r)h(r, 0) = (1 - r^2)/2$ corresponding to $R = 1$, and the arrows indicate the directions of increasing R .

imbibition ϕh is a monotonically decreasing function of r that takes its maximum value at the centre of the droplet according to $\phi h = O(1) = R^{-1/2}/2$ as $r \rightarrow 0^+$ and is non-zero at the contact line according to $\phi h = O(1) = (R^{-1/2} - R)/2$ as $r \rightarrow R^-$, and is a non-monotonic function of R (i.e., a non-monotonic function of t) near the centre of the droplet but a monotonically decreasing function of R (i.e., a monotonically increasing function of t) near the contact line. We note that this behaviour is qualitatively similar to that for a droplet on a finitely thick, anisotropic, flooded, porous substrate, and hence, we have not plotted ϕ and ϕh for this situation.

Physically, the contrast between the behaviour of ϕh for pure evaporation and imbibition behaviour of ϕh at the contact line is due to the advection of particles towards the contact line being balanced by the mass flux of particles into the distributed deposit for pure evaporation, whereas for pure imbibition the advection of particles towards the centre of the droplet exceeds the mass flux of particles into the distributed deposit. Furthermore, Figure 5.19(b) illustrates that for simultaneous evaporation and imbibition ϕh is always zero at the contact line, as the evaporation contribution to advection always dominates as $r \rightarrow R^-$, as discussed in Section 4.3.3, and hence so long as $\mathcal{E} > 0$ the advection of particles towards the contact line is balanced by the

mass flux of particles transferred to the distributed deposit. In particular, $\phi h \rightarrow 0^+$ everywhere within the droplet as $R \rightarrow 0^+$ for pure evaporation (i.e., as $t \rightarrow t_{\text{CA,E}}^-$), as discussed in Section 5.2.2. In contrast, $\phi h \rightarrow \infty$ everywhere within the droplet as $R \rightarrow 0^+$ for pure imbibition (i.e., as $t \rightarrow t_{\text{CA,I}}^-$). Physically, particles are swept inwards and towards the centre of the droplet for pure imbibition, as discussed in Section 4.3.2. However, the contact line recedes at a faster rate than the maximum inward velocity, $|dR/dt| = 4|\bar{u}(R, t)|$, and hence all of the particles are eventually captured by the contact line, and in this mode are eventually transferred to the distributed deposit in $0 \leq r < 1$. For simultaneous evaporation and imbibition the behaviour of ϕh will depend on both the nature and strength of physical mechanism(s) driving the mass loss from the droplet, with evaporation contributions dominating at the contact line and imbibition contributions dominating at the centre of the droplet, respectively. Nevertheless, all of the particles eventually leave the droplet, and in this mode are eventually transferred to the distributed deposit in $0 \leq r < 1$.

We find that M_{drop} and M_{dist} must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition. Substituting the expression for $r_0(R, t)$ given by (5.57) into (2.80) and (2.87) shows that for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate M_{drop} and M_{dist} are given by

$$M_{\text{drop}} = M_0 \left[1 - (1 - R^{3/2})^2 \right] \quad (5.63)$$

and

$$M_{\text{dist}} = M_0 \left[(1 - R^{3/2})^2 \right], \quad (5.64)$$

respectively, together with $M_{\text{ring}} \equiv 0$ (see, for example, D'Ambrosio *et al.* [84]) where (5.63) and (5.64) were given in the context of a droplet undergoing pure evaporation according to a spatially uniform local evaporative mass flux, as discussed in Section 1.8.2). Figures 5.17(b) and 5.18(b) shows the evolutions of M_{drop}/M_0 and M_{dist}/M_0 plotted as functions of t/t_{CA} for a range of values of $\mathcal{I}$ for a droplet undergoing simul-

taneous evaporation and imbibition on a finitely thick, anisotropic, dry and flooded, porous substrate, respectively. In particular, Figures 5.17(b) and 5.18(b) illustrate that, similarly to that discussed in Section 5.2.2, all of the particles initially within the droplet are eventually transferred to the distributed deposit in $0 \leq r < 1$.

We find that ϕ_{dist} must be evaluated numerically for a droplet undergoing simultaneous evaporation and imbibition. Substituting the expressions for h , r_0 , and ϕ given by equations (2.8), (5.56), and (5.61), respectively, into (2.88) shows that for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate ϕ_{dist} is given by

$$\phi_{\text{dist}} = \frac{3}{8r^{1/2}}(1 - r^{3/2}) \quad (5.65)$$

(see Freed-Brown [66] and D'Ambrosio *et al.* [84]) where (5.65) was given in the context of a droplet undergoing pure evaporation according to a spatially uniform local evaporative mass flux, as discussed in Section 1.8.2. In contrast to Section 4.3.2, the final density of the distributed deposit ϕ_{dist} is dependent on the values of $\mathcal{E}$ and $\mathcal{I}$, i.e., is dependent on both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet. However, we note that had we described the local evaporative mass flux as spatially uniform then this would not be the case and the final density of the distributed deposit ϕ_{dist} (but not, of course, the temporal evolution towards it) would be independent of the values of $\mathcal{E}$ and $\mathcal{I}$, i.e., would be independent of both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet.

Figure 5.20(a) shows ϕ_{dist} plotted as a function of r for pure evaporation (dashed line), simultaneous evaporation and imbibition $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$ (solid lines), and pure imbibition (dotted line) on a finitely thick, anisotropic, initially dry, porous substrate. In particular, Figure 5.20(a) illustrates that the final deposit does not, as one might have naively expected, always lie between the two distinguished limits of a droplet undergoing pure evaporation or pure imbibition, as the interplay between outward, inward, and zero regions of flow influences the nature of the final deposit. Furthermore, Figure 5.20(a) illustrates that $\phi_{\text{dist}} \rightarrow 0^+$ at the centre of the

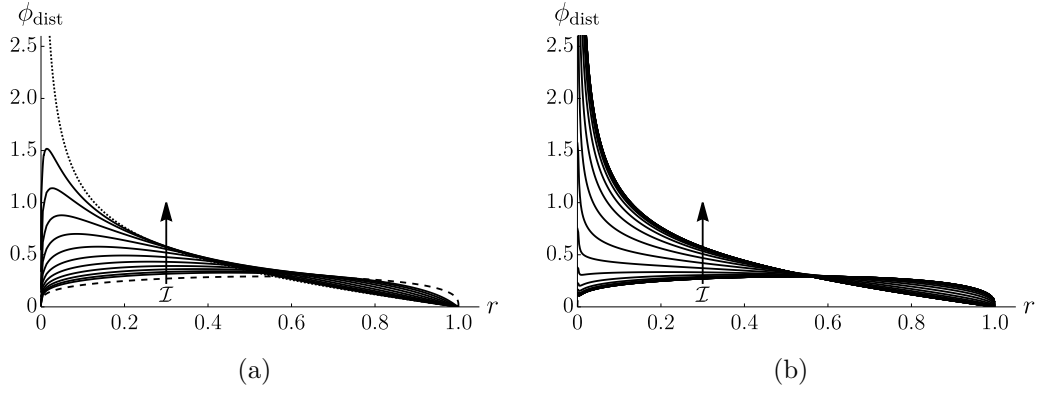


Figure 5.20: ϕ_{dist} in the CA mode plotted as a function of r for simultaneous evaporation and imbibition on a (a) finitely thick, anisotropic, initially dry, porous substrate ($\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$) and (b) finitely thick, anisotropic, flooded, porous substrate ($\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -15, -14, \dots, 15$). The dashed and dotted lines indicate the pure evaporation and imbibition solutions given by (5.26) and (5.65) respectively.

droplet, this is due to the evaporation contributions dominating the mean flow at later times, and hence there are larger regions of outwards flow (than those of inwards and zero flow, respectively) and the nature of the final deposit tends towards that of pure evaporation (i.e., a cleaved near-uniform deposit), as $t \rightarrow t_{\text{CA}}^-$.

Figure 5.20(b) shows ϕ_{dist} plotted as a function of r for pure evaporation (dashed line), simultaneous evaporation and imbibition $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$ (solid lines), and pure imbibition (dotted line) on a finitely thick, anisotropic, flooded, porous substrate. In particular, Figure 5.20(b) illustrates that, similarly to that on a finitely thick, anisotropic, initially dry, porous substrate, the final deposit does not, as one might have naively expected, always lie between the two distinguished limits of a droplet undergoing pure evaporation or pure imbibition, as the interplay between outwards, inwards, and zero regions of flow influences the nature of the final deposit. Furthermore, Figure 5.20(b) illustrates that, in contrast to that on a finitely thick, anisotropic, initially dry, porous substrate, $\phi_{\text{dist}} \rightarrow \infty$ at the centre of the droplet, this is due to the imbibition contributions dominating the mean flow at later times, and hence there are larger regions of inwards flow (than those of outwards and zero flow, respectively) and the nature of the final deposit tends towards that of pure imbi-

tion (i.e., a peak deposit), as $t \rightarrow t_{\text{CA}}^-$. For simultaneous evaporation and imbibition the behaviour of ϕ_{dist} will depend on both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet. Nevertheless, we find that the nature of the final deposit transitions from a cleaved near-uniform deposit (pure evaporation) to a peak deposit (pure imbibition). More generally, the nature of the final deposit spans a range of various final deposits, including cleaved near-uniform, near-uniform/uniform, volcano, dome, and peak, as sketched in Figures 1.7(e,f,g,h,i), respectively.

5.3.3 SS Mode

For a droplet undergoing simultaneous evaporation and imbibition the transport and deposition of particles must be evaluated numerically, as discussed in Section 5.1. In particular, for a droplet undergoing pure imbibition in the SS mode, the characteristic equations are given by (5.3) in the CR phase for $0 \leq t \leq t^*$ and (5.14) in the CA phase for $t^* < t \leq t_{\text{SS}}$. Hence the solution for r_0 is given by (5.4) in the CR phase and (5.15) in the CA phase. For a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate the solution for t_{ring} in the CR phase is given by (5.49) for $0 \leq t \leq t^*$ and t_{dist} in the CA phase is given by

$$t_{\text{dist}} = \frac{1}{32} \left[\left(2 - 3r_0^{4/3} \right) \theta^* + 1 \right]^2 \quad (5.66)$$

for $t^* < t \leq t_{\text{SS}}$, while for a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate the solution for t_{ring} in the CR phase is given by (5.50) for $0 \leq t \leq t^*$ and t_{dist} in the CA phase is given by

$$t_{\text{dist}} = \frac{1}{16} \left[3 \left(1 - r_0^{8/3} \right) - 2 \log \theta^* \right] \quad (5.67)$$

for $t^* < t \leq t_{\text{SS}}$. Figures 5.21 and 5.22 show (a) $t_{\text{ring}}/t_{\text{SS}}$ and (b) $t_{\text{dist}}/t_{\text{SS}}$ plotted as a function of r_0 for a range of values of θ^* for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry and flooded, porous substrate in the CR phase and CA phase of the SS mode. In particular, Figures 5.21 and 5.22 illustrate that

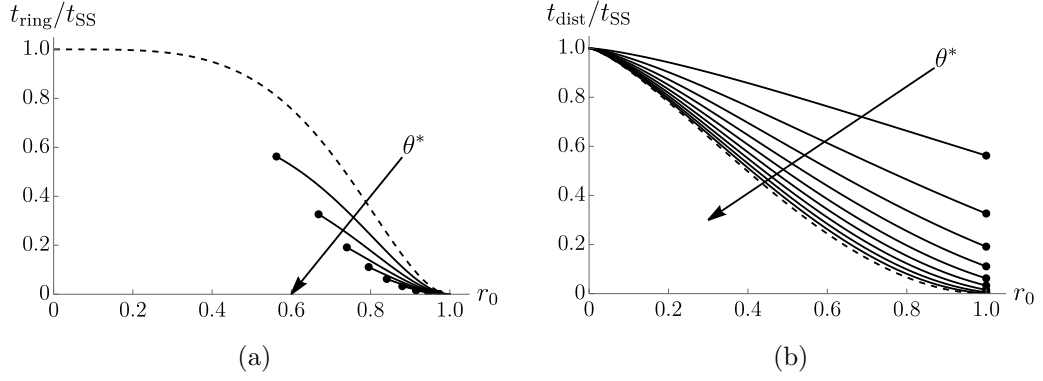


Figure 5.21: (a) $t_{\text{ring}}/t_{\text{SS}}$ given by (5.49) and (b) $t_{\text{dist}}/t_{\text{SS}}$ given by (5.66) plotted as functions of r_0 for a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate, for $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed lines in (a,b) indicate the CR and CA mode solutions for $t_{\text{ring}}/t_{\text{CR}}$ and $t_{\text{dist}}/t_{\text{CA}}$, respectively. The arrows indicate the directions of increasing θ^* .

both quantities inherit their corresponding behaviours in the CR and CA modes in the corresponding phases.

Solving for ϕ yields (5.51) in the CR phase and

$$\phi = \frac{(1 - r_0^2) (\theta^{*-1/2} - r_0^2 R^{1/2})}{(R^{3/2} - r_0^2) (1 - r_0^2 R^{1/2})} \quad (5.68)$$

in the CA phase for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate. Hence ϕ is given by (5.52) in the CR phase and

$$\phi = \frac{(R^{1/2} - r^2) (1 - r^2 \theta^{*1/2})}{(1 - r^2) \theta^{*1/2} (R^2 - r^2)} \quad (5.69)$$

in the CA phase, and ϕh is given by (5.53) in the CR phase and

$$\phi h = \frac{\theta^{*1/2} (R^{1/2} - r^2) (1 - r^2 \theta^{*1/2})}{2 (1 - r^2) R} \quad (5.70)$$

in the CA phase. Figure 5.23 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of θ in the CR phase and R in the CA phase for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate. In particular, Figure 5.23 illustrates that both quantities inherit their corresponding be-

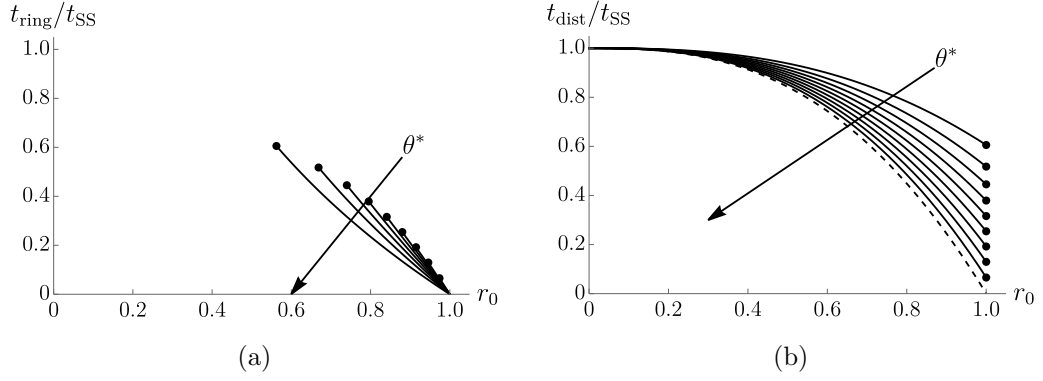


Figure 5.22: (a) $t_{\text{ring}}/t_{\text{SS}}$ given by (5.50) and (b) $t_{\text{dist}}/t_{\text{SS}}$ given by (5.67) plotted as functions of r_0 for a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate, for $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed line in (b) indicates the CA mode solution for $t_{\text{dist}}/t_{\text{CA}}$. The arrows indicate the directions of increasing θ^* .

haviours in the CR and CA modes in the corresponding phases. In particular, $\phi h \rightarrow \infty$ everywhere within the droplet as $R \rightarrow 0^+$, i.e., as $t \rightarrow t_{\text{SS,I}}^-$. Physically, as in the CA mode and discussed in Section 5.3.2, particles are swept inwards and towards the centre of the droplet for pure imbibition. However, the contact line recedes at a faster rate than the maximum inward velocity, $|dR/dt| = 4|\bar{u}(R, t)|$, and hence all of the particles are eventually captured by the contact line in the CA phase showing that all of the particles eventually leave the droplet, and in this mode are eventually transferred to either the ring deposit at $r = 1$ or the distributed deposit in $0 \leq r < 1$.

M_{drop} , M_{ring} and M_{dist} are given by (5.54), (5.55) and $M_{\text{dist}} \equiv 0$ in the CR phase, and by

$$M_{\text{drop}} = M_0 \left[2R\theta^{*1/2} - R\theta^*(R^2 - 2R^{1/2} + 2) + \frac{2\theta^{*1/2}}{R} \left\{ (1 - R^{1/2})(1 - \theta^{*1/2}) \log(1 - R^2) \right\} \right], \quad (5.71)$$

$$M_{\text{ring}} \equiv M_{\text{ring}}(t^*) = M_0 \left[1 - (2\theta^{*1/2} - \theta^*) \right], \quad (5.72)$$

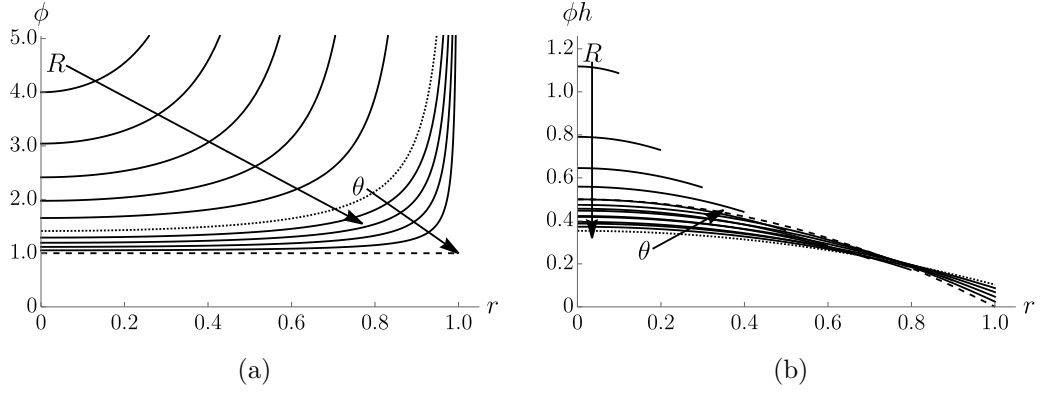


Figure 5.23: (a) ϕ given by (5.52) and (5.69) and (b) ϕh given by (5.53) and (5.70) in the SS mode plotted as functions of r for $\theta = 3/5, 7/10, 4/5, 9/10$ in the CR phase and $R = 1/10, 1/5, \dots, 9/10$ in the CA phase when $\theta^* = 1/2$. The dashed lines indicate the initial values $\phi_0(r) \equiv 1$ and $\phi_0(r)h(r, 0) = (1 - r^2)/2$ corresponding to $\theta = 1$, the dotted lines indicate the solution at $t = t^*$ corresponding to $\theta = \theta^* = 1/2$, and the arrows indicate the directions of increasing θ and R .

and

$$M_{\text{dist}} = M_0 \left[-2R\theta^{*1/2} + R\theta^* \left(R^2 - 2R^{1/2} + 2 \right) - \frac{2\theta^{*1/2}}{R} \left\{ (1 - R^{1/2})(1 - \theta^{*1/2}) \log(1 - R^2) \right\} + 2\theta^{*1/2} - \theta^* \right], \quad (5.73)$$

in the CA phase for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate. Figures 5.24(a,b,c) show the evolutions of (a) M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{dist}/M_0 plotted as functions of t/t_{SS} for pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate for a range of values of θ^* , while Figure 5.24(d) shows the final (scaled) masses in the deposit ring, $M_{\text{ring}}(t_{\text{SS}})/M_0 (= M_{\text{ring}}(t^*)/M_0)$, and in the distributed deposit, $M_{\text{dist}}(t_{\text{SS}})/M_0$, plotted as functions of θ^* for pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate. In particular, Figure 5.24(d) illustrates that there is a greater mass of particles in the final deposit ring than in the final distributed deposit (i.e., $M_{\text{ring}}(t_{\text{SS}}) > M_{\text{dist}}(t_{\text{SS}})$) when $0 \leq \theta^* < \theta_{\text{crit}}^*$, and vice versa (i.e., $M_{\text{ring}}(t_{\text{SS}}) < M_{\text{dist}}(t_{\text{SS}})$) for $\theta_{\text{crit}}^* < \theta^* \leq 1$, where $\theta_{\text{crit}}^* = 3/2 - 2^{1/2} \simeq 0.0858$ is the critical value of θ^* for which $M_{\text{ring}}(t_{\text{SS}})/M_0 = M_{\text{dist}}(t_{\text{SS}})/M_0 = 1/2$. Figures 5.25(a,b,c) show the evolutions of (a)

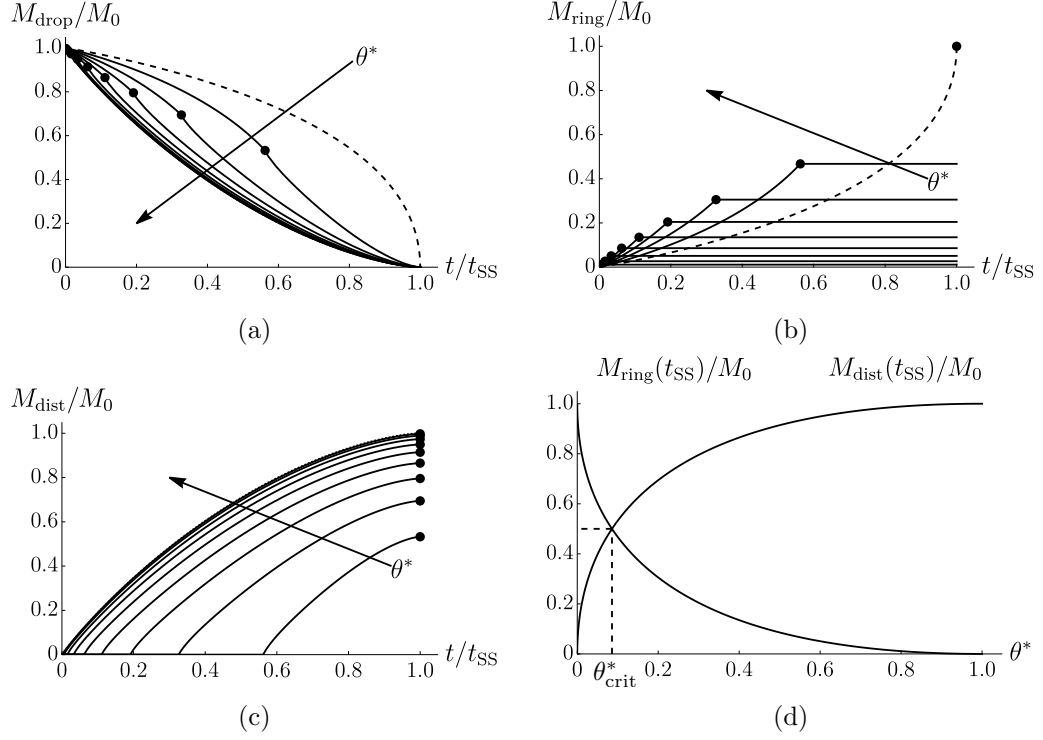


Figure 5.24: The evolutions of (a) M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{dist}/M_0 in the SS mode plotted as functions of t/t_{SS} for pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate when $\theta^* = 1/10, 1/5, \dots, 9/10$. The dots in (a) denote the time at which the CR phase ends, i.e., $t = t^*$. (d) $M_{\text{ring}}(t_{\text{SS}})/M_0 (= M_{\text{ring}}(t^*)/M_0)$ and $M_{\text{dist}}(t_{\text{SS}})/M_0$ in the SS mode plotted as functions of θ^* for pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate. The dashed lines in (a,b) indicate the CR mode solutions for M_{drop}/M_0 and M_{ring}/M_0 , respectively, and the dashed lines in (d) indicate the critical value of $\theta^* = \theta^*_{\text{crit}} = 3/2 - 2^{1/2} \simeq 0.0858$ for which $M_{\text{ring}}(t_{\text{SS}})/M_0 = M_{\text{dist}}(t_{\text{SS}})/M_0 = 1/2$. The dotted lines in (a,c) indicate the CA mode solutions for M_{drop}/M_0 and M_{dist}/M_0 , respectively. The arrows indicate the directions of increasing θ^* .

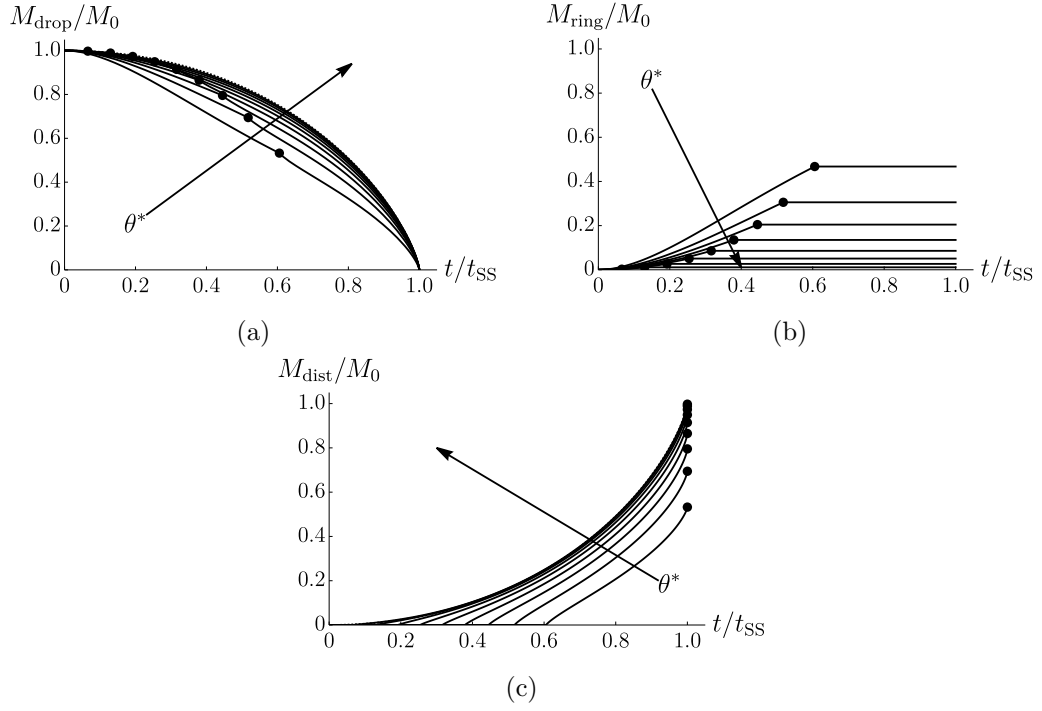


Figure 5.25: The evolutions of (a) M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{dist}/M_0 in the SS mode plotted as functions of t/t_{SS} for pure imbibition on a finitely thick, anisotropic, flooded, porous substrate when $\theta^* = 1/10, 1/5, \dots, 9/10$. The dots in (a) denote the time at which the CR phase ends, i.e., $t = t^*$. The dashed lines in (a,b) indicate the CR mode solutions for M_{drop}/M_0 and M_{ring}/M_0 , respectively. The dotted lines in (a,c) indicate the CA mode solutions for M_{drop}/M_0 and M_{dist}/M_0 , respectively. The arrows indicate the directions of increasing θ^* .

M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{dist}/M_0 plotted as functions of t/t_{SS} for pure imbibition on a finitely thick, anisotropic, flooded, porous substrate for a range of values of θ^* .

Substituting the expressions for h , r_0 , and ϕ given by equations (2.8), (5.56), and (5.69), respectively, into (2.92) shows that in the CA phase of the SS mode ϕ_{dist} is given by

$$\phi_{\text{dist}} = \frac{3\theta^* (\theta^{*-1/2} - r^2) (1 - r^{3/2})}{8r^{1/2} (1 - r^2)}. \quad (5.74)$$

Figure 5.26 shows ϕ_{dist} given by (5.74) plotted as a function of r for a range of values of θ^* , including the solution in the CA mode given by (5.65) corresponding to $\theta^* = 1$. In particular, Figure 5.26 illustrates that the final density of the distributed deposit in

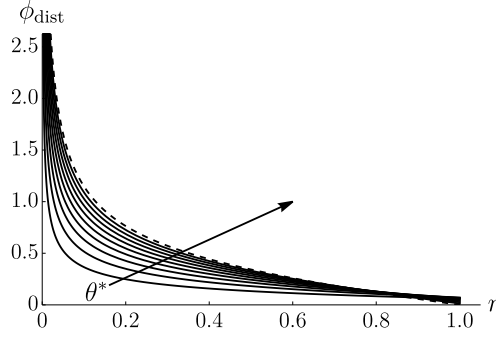


Figure 5.26: ϕ_{dist} given by (5.74) in the CA phase of the SS mode plotted as a function of r for $\theta^* = 1/10, 1/5, \dots, 9/10$. The dashed line indicates the solution in the CA mode given by (5.65) corresponding to $\theta^* = 1$, and the arrow indicates the directions of increasing θ^* .

the SS mode tends to infinity at the centre of the droplet and takes its minimum value of $\phi_{\text{dist}} = (9/32) (\theta^* - \theta^{*1/2})$ at $r = 1$ (i.e., at the initial position of the contact line). Note that, as in the CA mode and discussed in Section 5.3.2, a peak deposit forms in the CA phase of the SS mode for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate.

5.3.4 SJ Mode

For a droplet evolving in the SJ mode, the characteristic equations are given by (5.3) in the n th CR phase for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Hence the solution for $r_{0,n}$ for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate is

$$r_{0,n} = r \left(\frac{\theta}{\theta_{\text{max}}} \right)^{1/4} \quad (5.75)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Setting $r = R_n$ shows that

$$r_{0,n}(R_n, t) = R_n \left(\frac{\theta}{\theta_{\text{max}}} \right)^{1/4} \quad (5.76)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). In particular, for a droplet undergoing pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate the solution

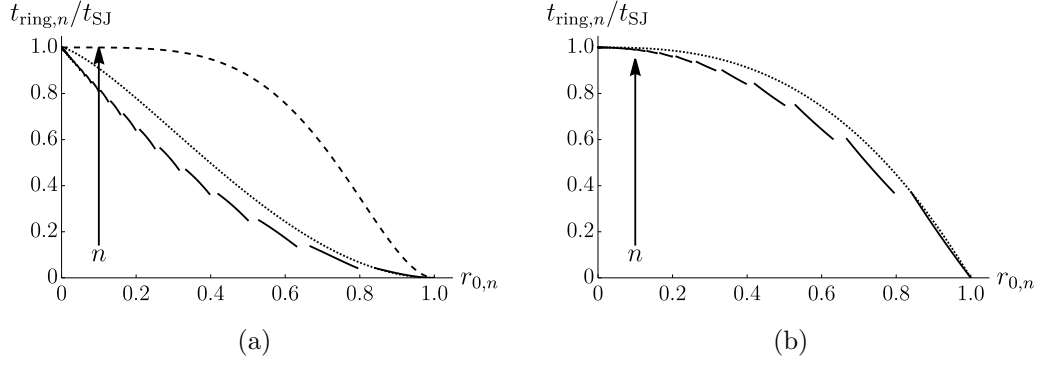


Figure 5.27: $t_{\text{ring},n}/t_{\text{SJ}}$ plotted as functions of $r_{0,n}$ in each CR phase for pure imbibition on a (a) finitely thick, anisotropic, initially dry, porous substrate and (b) finitely thick, anisotropic, flooded, porous substrate when $\theta_{\min} = 1/2$. The dashed and dotted lines in (a,b) indicate the CR and CA mode solutions for $t_{\text{ring}}/t_{\text{CR}}$ and $t_{\text{dist}}/t_{\text{CA}}$, respectively. The arrows indicate the directions of increasing n .

for $t_{\text{ring},n}$ is given by

$$t_{\text{ring},n} = \left[\frac{R_n}{4(2)^{1/2}} \left\{ 1 - \left(\frac{r_{0,n}}{R_n} \right)^4 \right\} + t_{n-1}^{1/2} \right]^2 \quad (5.77)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), while for a droplet undergoing pure imbibition on a finitely thick, anisotropic, flooded, porous substrate the solution for $t_{\text{ring},n}$ is given by

$$t_{\text{ring},n} = t_{n-1} - \frac{R_n^2}{2} \log \left(\frac{r_0}{R_n} \right) \quad (5.78)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Figure 5.27 shows $t_{\text{ring},n}/t_{\text{SJ}}$ plotted as functions of $r_{0,n}$ in each CR phase for pure imbibition on a (a) finitely thick, anisotropic, initially dry, porous substrate and (b) finitely thick, anisotropic, flooded, porous substrate when $\theta_{\min} = 1/2$. In particular, Figure 5.27 illustrates that $t_{\text{ring},n}$ inherits the corresponding behaviour in the CR mode in each CR phase, i.e., particles that are initially near the n th contact line are deposited (in the n th ring deposit) before those that are initially near the centre of the droplet.

Solving for ϕ in the n th CR phase for a droplet undergoing pure imbibition on a

finitely thick, anisotropic, dry or flooded, porous substrate yields

$$\phi = \phi_{n,\max}(r_{0,n}) \left[\frac{\left(1 - \frac{r_{0,n}^2}{R_n^2}\right)^2 \left(\frac{\theta}{\theta_{\max}}\right)}{\left(\frac{\theta}{\theta_{\max}} - \frac{r_{0,n}^2}{R_n^2}\right)^2} \right] \quad (5.79)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) where $\phi_{n,\max}(r_{0,n}) = \phi(r_{0,n-1}, t_{n-1})$ denotes the concentration of particles within the droplet at the end of the $(n-1)$ th CR phase.

Hence ϕ is given by

$$\phi = \frac{\theta^{-1/2} R_n^{-3/2} - \frac{r^2}{R_n^2}}{1 - \frac{r^2}{R_n^2}} \quad (5.80)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) and ϕh is given by

$$\phi h = \frac{\theta R_n}{2} \left(\theta^{-1/2} R_n^{-3/2} - \frac{r^2}{R_n^2} \right) \quad (5.81)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$). Figure 5.28 shows (a) ϕ and (b) ϕh plotted as functions of r for a range of values of θ in each CR phase. In particular, Figure 5.28 illustrates that both quantities inherit their corresponding behaviour in the CR mode in each CR phase. However, in contrast to the CR mode, ϕh is a monotonically increasing function of n everywhere within the droplet that takes its maximum value at the centre of the droplet according to $\phi h = O(1) = \theta^{1/2} R_n^{-1/2}/2$ as $r \rightarrow 0^+$ and is non-zero at the n th contact line according to $\phi h = O(1) = (\theta^{1/2} R_n^{-1/2} - \theta R_n)/2$ as $r \rightarrow R_n^-$. In particular, in contrast to a droplet undergoing pure imbibition on an infinitely thick, isotropic, flooded, porous substrate in the SJ mode, as discussed in Section 5.2.4, $\phi h \rightarrow \infty$ everywhere within the droplet as $t \rightarrow t_{\text{SJ}}^-$, however, all of the particles eventually leave the droplet, and in this mode are eventually transferred to the (theoretically infinite number of) ring deposits at $r = R_n$ ($n = 1, 2, 3, \dots$).

M_{drop} and $M_{\text{ring},n}$ are given by

$$M_{\text{drop}} = M_0 \left(2R_n^{3/2} \theta^{1/2} - R_n^3 \theta \right) \quad (5.82)$$

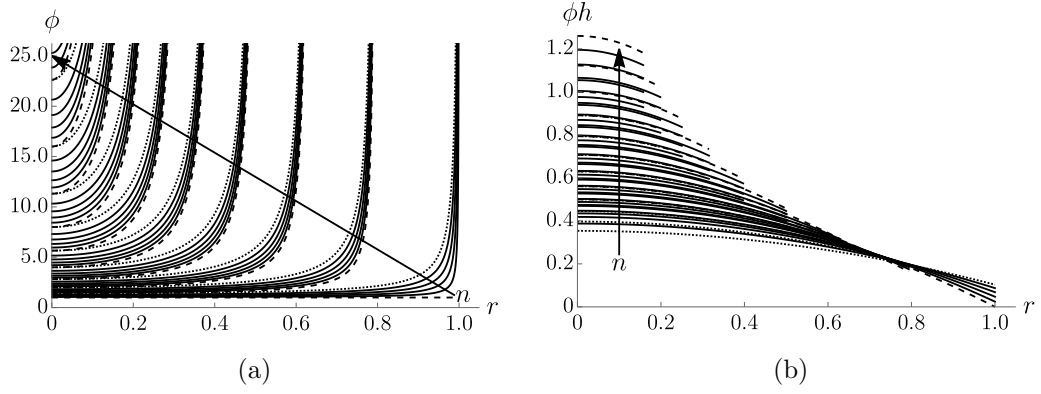


Figure 5.28: (a) ϕ given by (5.80) and (b) ϕh given by (5.81) in the SJ mode plotted as functions of r at $\theta = 3/5, 7/10, 4/5, 9/10$ in each CR phase when $\theta_{\min} = 1/2$. The dashed and the dotted lines indicate the values at $t = t_{n-1}$ and $t = t_n$ ($n = 1, 2, 3, \dots$) (i.e., at the start and the end of each CR phase) corresponding to $\theta = \theta_{\max} = 1$ and $\theta = \theta_{\min} = 1/2$, respectively, and the arrows indicate the directions of increasing n .

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$) and

$$M_{\text{ring},n} = M_0 \left[2R_n^{3/2} \left(\theta_{\max}^{1/2} - \theta^{1/2} \right) - R_n^3 (\theta_{\max} - \theta) \right] \quad (5.83)$$

for $t_{n-1} < t < t_n$ ($n = 1, 2, 3, \dots$), together with M_{rings} , which is determined by summing the non-zero values of $M_{\text{ring},n}$, and $M_{\text{dist}} \equiv 0$. Figures 5.29(a,b) show the evolutions of (a) M_{drop}/M_0 and (b) M_{rings}/M_0 plotted as functions of t/t_{SJ} for pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate when $\theta_{\min} = 1/2$, while Figure 5.29(c) shows the final (scaled) mass of particles in the n th deposit ring, $M_{\text{ring},n}(t_{\text{SJ}})/M_0 (= M_{\text{ring},n}(t_n)/M_0)$, plotted as a function of $\theta_{\min}$ for $n = 1, 2, 3, \dots$ for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate. In particular, Figure 5.29(c) illustrates that $M_{\text{ring},n}(t_{\text{SJ}})$ decreases monotonically with n for $0 \leq \theta_{\min} \leq \theta_{\min,\text{crit}} = 3 - 2^{3/2} \simeq 0.1716$, but is non-monotonic for $\theta_{\min,\text{crit}} \leq \theta_{\min} \leq 1$. Figures 5.30(a,b) show the evolutions of (a) M_{drop}/M_0 and (b) M_{rings}/M_0 plotted as functions of t/t_{SJ} for pure imbibition on a finitely thick, anisotropic, flooded, porous substrate when $\theta_{\min} = 1/2$.

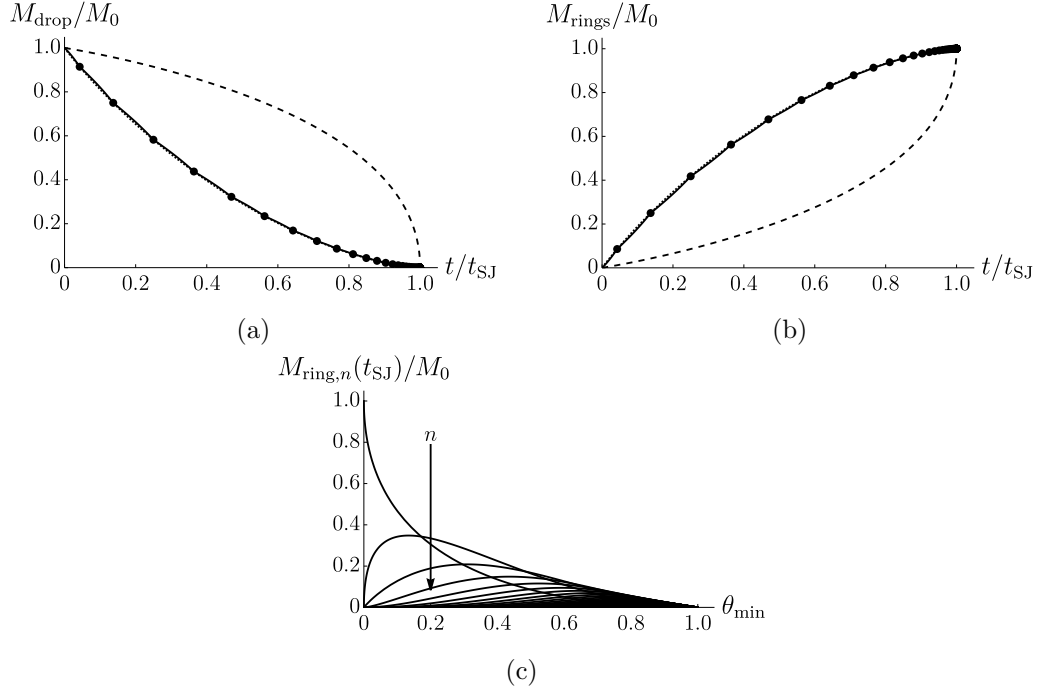


Figure 5.29: The evolutions of (a) M_{drop}/M_0 and (b) M_{rings}/M_0 in the SJ mode plotted as functions of t/t_{SJ} for pure imbibition on a finitely thick, anisotropic, initially dry, porous substrate when $\theta_{\text{min}} = 1/2$. The dots in (a) and (b) denote the times at which the n th CR phase ends, i.e., $t = t_n$ ($n = 1, 2, 3, \dots$). (c) $M_{\text{ring},n}(t_{\text{SJ}})/M_0$ ($= M_{\text{ring},n}(t_n)/M_0$) in the SJ mode plotted as a function of θ_{min} for $n = 1, 2, 3, \dots$. The dashed lines in (a,b) indicate the CR mode solutions for M_{drop}/M_0 and M_{ring}/M_0 , respectively. The dotted lines in (a,c) indicate the CA mode solutions for M_{drop}/M_0 and M_{dist}/M_0 , respectively. The arrows indicate the directions of increasing n .

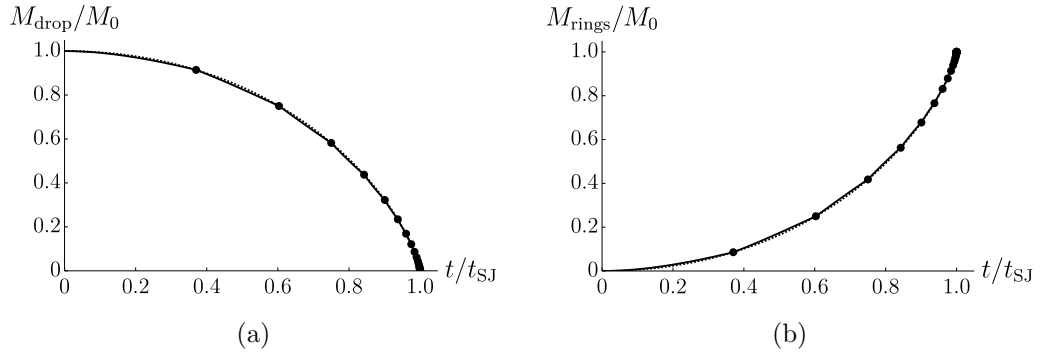


Figure 5.30: The evolutions of (a) M_{drop}/M_0 and (b) M_{rings}/M_0 in the SJ mode plotted as functions of t/t_{SJ} for pure imbibition on a finitely thick, anisotropic, flooded, porous substrate when $\theta_{\text{min}} = 1/2$. The dots in (a) and (b) denote the times at which the n th CR phase ends, i.e., $t = t_n$ ($n = 1, 2, 3, \dots$). The dotted lines indicate the CA mode solutions for M_{drop}/M_0 and M_{dist}/M_0 , respectively.

5.4 Conclusions

In Chapter 5 we have analysed mathematical models for the transport and deposition of particles within the droplet and onto the substrate in the CR, CA, SS, and SJ modes in the regime in which diffusion of particles is faster than axial advection but slower than radial advection of particles.

In Section 5.2 we determined the transport and deposition of particles within the droplet and onto an infinitely thick, isotropic, flooded, porous substrate in the CR, CA, SS, and SJ modes, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.1, respectively. We showed that in this situation the final deposit from a droplet evolving in the CR, CA, SS, and SJ modes (namely a ring deposit, a distributed deposit, a combined ring and distributed deposit, and multiple ring deposits, respectively) is independent of both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet. Furthermore, we showed that the distributed deposit in this situation is a cleaved near-uniform deposit in the CA mode and the CA phase of the SS mode, respectively.

In Section 5.3 we determined the transport and deposition of particles within the droplet and onto a finitely thick, anisotropic, dry or flooded, porous substrate in the CR and CA modes, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.2 or 2.7.3, respectively. In contrast to Section 5.2, we showed that in this situation the final deposit from a droplet evolving in the CR and CA modes (namely a ring deposit and a distributed deposit, respectively) is dependent on both the nature and the strength of the physical mechanism(s) driving the mass loss from the droplet, and that the final deposit in the CA mode encompasses a cleaved near-uniform deposit, near-uniform/uniform deposit, volcano deposit, dome deposit, and peak deposit. Furthermore, we showed that for a droplet undergoing pure imbibition on a finitely thick, anisotropic, dry or flooded, porous substrate that the distributed deposit is a peak deposit in the CA mode and the CA phase of the SS mode.

The results described in Chapter 5 indicate that, as shown experimentally (see, for example, Dou and Derby [187] and Li *et al.* [6]), evaporation and imbibition have the

same qualitative effect on the transport of particles in the CR mode, with the evolution towards the ring deposit based on the relative strength of evaporation and/or imbibition. We have also demonstrated that the quantitative differences in the local imbibition mass flux, as described in Sections 2.7.1, 2.7.2, and 2.7.3, lead to the same final deposits in the CA mode as those obtained when contrasting a diffusion-limited local evaporative mass flux with a spatially uniform equivalent, namely a cleaved near-uniform and peaked final deposit, respectively. Furthermore, we showed that for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, initially dry, porous substrate the evaporation contributions to the mean flow dominate at late times, and hence, the final deposit is always cleaved at the centre, while for a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, flooded, porous substrate the imbibition contributions to the mean flow dominate at late times, and hence, the final deposit is always peaked at the centre. We note that the transport and deposition of particles could be experimentally investigated using the methods discussed in Section 1.2, providing experimental routes to verify and validate the analytical expressions and numerical results determined in Chapter 5. Moreover, the finding that a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate and finitely thick, anisotropic, dry or flooded, porous substrate leads to a different final deposit provides a useful tool to control the final deposit. Having determined the transport and deposition of particles in the regime in which diffusion of particles is faster than axial advection but slower than radial advection of particles, in Chapter 6 we consider the alternative regime in which diffusion of particles is slower than both radial and axial advection of particles and compare the behaviours in each regime.

Chapter 6

Particle Paths

6.1 Overview

In Chapter 5, we considered the transport of, and deposition onto the substrate of, the particles in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$ in which diffusion of particles is faster than axial advection but slower than radial advection of particles, and hence at leading order axial diffusion causes the concentration of particles to be independent of z . In this chapter, we calculate the paths of the particles within the droplet in the alternative regime in which diffusion of particles is slower than both radial and axial advection of particles, and hence at leading order diffusion of particles plays no role and the transport of particles is purely advective. Specifically, we consider the regime in which the reduced Péclet number satisfies $\text{Pe}^* \gg 1$, and hence at leading order the path taken by any particle, denoted by $(r, z) = (r(t), z(t))$, is determined by solving

$$\frac{dr}{dt} = u \quad \text{and} \quad \frac{dz}{dt} = w \quad \text{for} \quad 0 \leq z \leq h \quad \text{and} \quad 0 \leq r \leq R, \quad (6.1)$$

subject to initial conditions of the form $(r(0), z(0)) = (r_0, z_0)$, where (r_0, z_0) is the initial position of the particle. Only the CR and CA modes will be considered in this chapter, however, in principle, such analysis could be extended to other modes (including the SS and SJ modes).

Following the same approach as Kang *et al.* [78], D'Ambrosio *et al.* [82], and Coombs *et al.* [182] we assume that if a particle reaches the (descending) free surface of the

droplet then it remains on it until the droplet has completely evaporated and/or imbibed. We refer to this as free-surface capture. Once a particle has been captured, it moves along the free surface according to

$$\frac{dr}{dt} = u \quad \text{and} \quad \frac{dz}{dt} = w - \mathcal{E}J_E = \frac{\partial h}{\partial t} + u \frac{\partial h}{\partial r} \quad \text{on} \quad z = h \quad \text{for} \quad 0 \leq r \leq R, \quad (6.2)$$

and is eventually transported to the contact line. We also assume that once a particle reaches the surface of the substrate it remains there (i.e., it does not enter the substrate or move along its surface) until the droplet has completely evaporated and/or imbibed. We refer to this as substrate capture. In addition, we assume that the presence of particles on the free surface does not disrupt the shape of the droplet or the flow within it, and that the presence of particles on the surface of the substrate does not inhibit the flow of liquid through it (this latter assumption could readily be relaxed in future work if required, as discussed in Chapter 7). Equations (6.1) and (6.2) must, in general, be solved numerically, which we implemented using Mathematica [238] routine `NDSolve[]`. Specifically, we used the method of lines and confirmed convergence under refinement by varying the discretisation parameters and ensuring that the resulting particle trajectories were insensitive to further tightening of the numerical tolerances.

In Sections 6.2, 6.3, and 6.4 we consider the particles paths in this regime for a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate, a finitely thick, anisotropic, initially dry, porous substrate, and finitely thick, anisotropic, flooded, porous substrate in the CR and CA modes.

6.2 An infinitely thick, isotropic, flooded, porous substrate

6.2.1 Particle Paths in the CR Mode

The equations governing the paths of the particles within a droplet evolving in the CR mode are obtained by substituting the expression for u given by (4.3) and the expres-

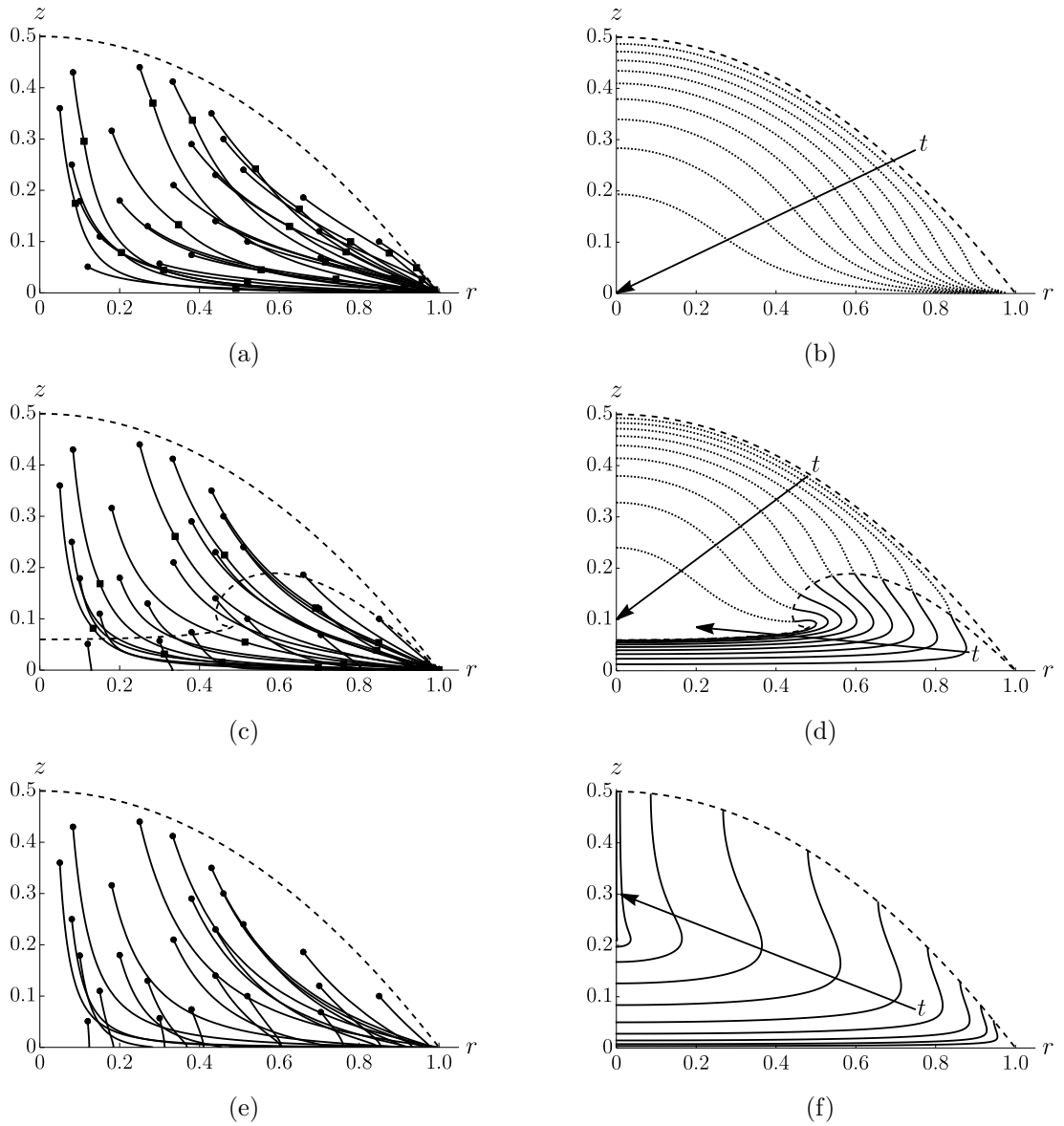


Figure 6.1: Plots of (a,c,e) the paths of a selection of representative particles and (b,d,f) the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) for a droplet evolving in the CR mode at $t = (1/10, 1/5, \dots, 9/10) \times t_{\text{CR}}$ for (a,b) pure evaporation and (c,d) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$, and at $t = 2^n \times \pi$ ($n = -10, -9, \dots, 0$) for (e,f) pure imbibition. In (a,c,e) the dots ($\bullet$) denote the initial positions of the particles and the squares ($\blacksquare$) denote the positions at which free-surface capture occurs. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dashed line in (c,d) indicates the critical watershed curve on which free-surface and substrate capture occur simultaneously, and the arrows in (b,d,f) indicate the directions of increasing t .

sion for w given by (4.4) into (6.1) and (6.2). Figures 6.1(a,c,e) show the paths of a selection of representative particles and Figures 6.1(b,d,f) show the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) at various times for (a,b) pure evaporation, (c,d) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$, and (e,f) pure imbibition. In particular, Figure 6.1 shows that in the regime $\text{Pe}^* \gg 1$ the particles are always advected by the flow within the droplet radially outwards (i.e., towards the contact line) and downwards (i.e., towards the substrate) and always captured by either the free surface or the substrate. Specifically, Figures 6.1(a,b) show that for pure evaporation all of the particles are eventually captured by the free surface and then transported to the contact line, forming a ring deposit at the (pinned) contact line, as sketched in Figure 2.7(a) (see, for example, D’Ambrosio *et al.* [82]). This behaviour is qualitatively the same as that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$, as discussed in Sections 2.8 and 5.2. On the other hand, Figures 6.1(e,f) show that for pure imbibition all of the particles are eventually captured by the substrate, forming a distributed deposit within the initial footprint of the droplet, as sketched in Figure 2.7(b). This behaviour is qualitatively different to that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$. Figures 6.1(c,d) show that for simultaneous evaporation and imbibition both kinds of capture occur and there is a critical “watershed” curve (i.e., a locus of initial positions of the particles) on which free-surface and substrate capture occur simultaneously and above which the particles are captured by the free surface and below which they are captured by the substrate, forming a combined ring and distributed deposit as sketched in Figure 2.7(c). Again, this behaviour is qualitatively different to that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$. The watershed curve was computed using two complementary procedures. First, we integrated the particle-path equations forward in time from a finely discretised set of initial positions across the droplet footprint and recorded whether each trajectory first intersected the free surface or the substrate. Second, we integrated the equations backwards in time from points located on the substrate surface at the droplet’s lifetime to determine their corresponding initial positions. Both approaches were repeated over a range of spatial and temporal discretisations, and we found that the resulting watershed curve was in-

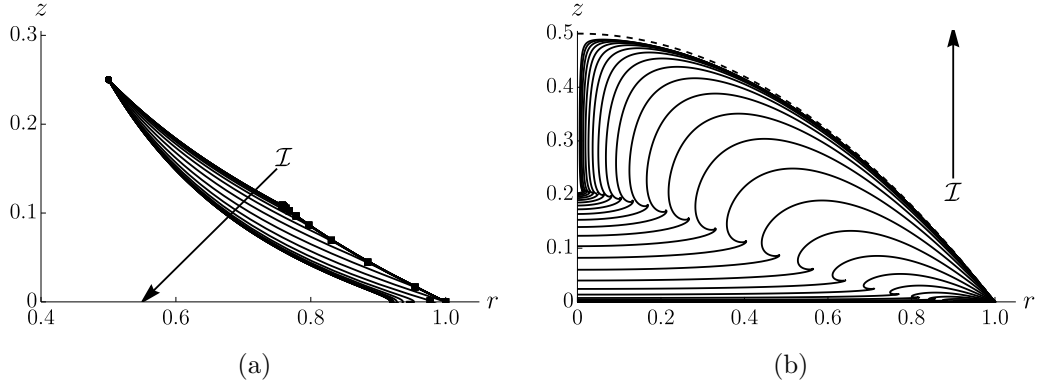


Figure 6.2: Plots of (a) the path of a representative particle and (b) the critical watershed curve for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -15, -14, \dots, 15$ within a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate in the CR mode. The dots and squares in (a) represent the initial position and the point at which free-surface capture occurs, respectively, for each representative particle. The dashed line in (b) indicates the initial free-surface profile of the droplet $h(r, 0) = (1 - r^2)/2$.

sensitive to further refinement, with no meaningful changes observed at the resolutions considered.

Figures 6.2(a,b) shows the paths of a representative particle and the critical watershed curve for a range of values of $\mathcal{I}$. In particular, Figures 6.2(a,b) shows that, as expected, increasing the strength of evaporation and/or imbibition (i.e., increasing $\mathcal{E}$ and/or $\mathcal{I}$) leads to a particle either being captured by the free surface or substrate. Furthermore, we find that the shape of the critical watershed curve is dependent on the relative strength of evaporation and/or imbibition and the locus of the initial positions of particles for which free surface and substrate capture occur simultaneously, as shown in Figure 6.1(d) for $\mathcal{E} = \mathcal{I} = 1$. Additionally, in this situation evaporation contributions dominate the flow at later times (i.e., as $t \rightarrow t_{\text{CR}}^-$), as discussed in Section 4.2.1. Hence, particles which are initially closer to the centre of the droplet are captured by the free surface.

6.2.2 Particle Paths in the CA Mode

The equations governing the paths of the particles within a droplet evolving in the CA mode are obtained by substituting the expression for u given by (4.18) and the

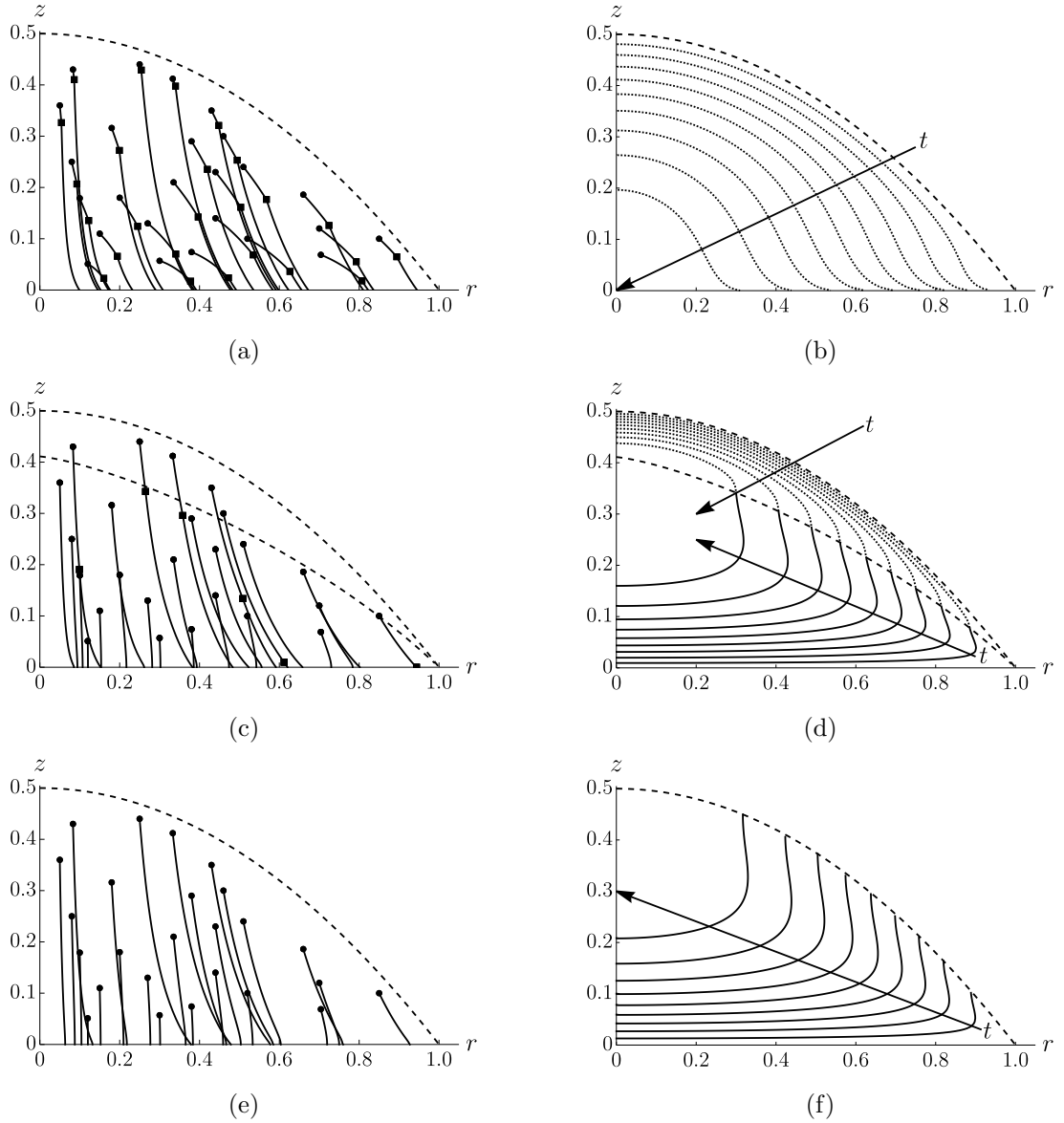


Figure 6.3: Plots of (a,c,e) the paths of a selection of representative particles and (b,d,f) the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) for a droplet evolving in the CA mode at $t = (1/10, 1/5, \dots, 9/10) \times t_{CA}$ for (a,b) pure evaporation, (c,d) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$, and (e,f) pure imbibition. In (a,c,e) the dots ($\bullet$) denote the initial positions of the particles, and in (a,c) the squares ($\blacksquare$) denote the positions at which free-surface capture occurs. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dashed line in (c,d) indicates the critical watershed curve on which free-surface and substrate capture occur simultaneously, and the arrows in (b,d,f) indicate the directions of increasing t .

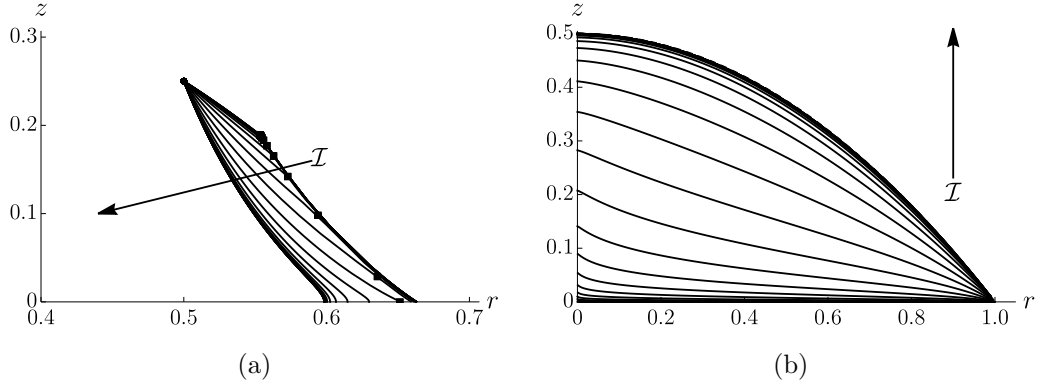


Figure 6.4: Plots of (a) the path of a representative particle and (b) the critical watershed curve for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -15, -14, \dots, 15$ within a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate in the CA mode. The dots and squares in (a) represent the initial position and the point at which free-surface capture occurs, respectively, for each representative particle. The dashed line in (b) indicates the initial free-surface profile of the droplet $h(r, 0) = (1 - r^2)/2$.

expression for w given by (4.19) into (6.1) and (6.2). Figure 6.3, which is analogous to Figure 6.1 but for a droplet evolving in the CA mode, shows that the particle paths are qualitatively the same as those for a droplet evolving in the CR mode (i.e., the particles are advected towards the (unpinned) contact line). However, the motion of the (unpinned) contact line means that the particles are always deposited as a distributed deposit within the initial footprint of the droplet, as sketched in Figure 2.7(b). This behaviour is qualitatively the same as that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$, as discussed in Sections 2.8 and 5.2.

Figures 6.4(a,b) shows the paths of a representative particle and the critical watershed curve for a range of values of $\mathcal{I}$. In particular, Figures 6.4(a,b) shows that the particle paths and the critical watershed curves are qualitatively the same as those for a droplet evolving in the CR mode and (again) that the critical watershed curve profile is dependent on the relative strength of evaporation and/or imbibition and the initial positions of particles for which free surface and substrate capture occur simultaneously, as shown in Figure 6.3(d) for $\mathcal{E} = \mathcal{I} = 1$, and that, in contrast to that discussed in Section 6.2.1, particles which are initially positioned closer to the centre of the droplet experience stronger imbibition contributions to the flow at later times (i.e., as $t \rightarrow t_{\text{CA}}^-$),

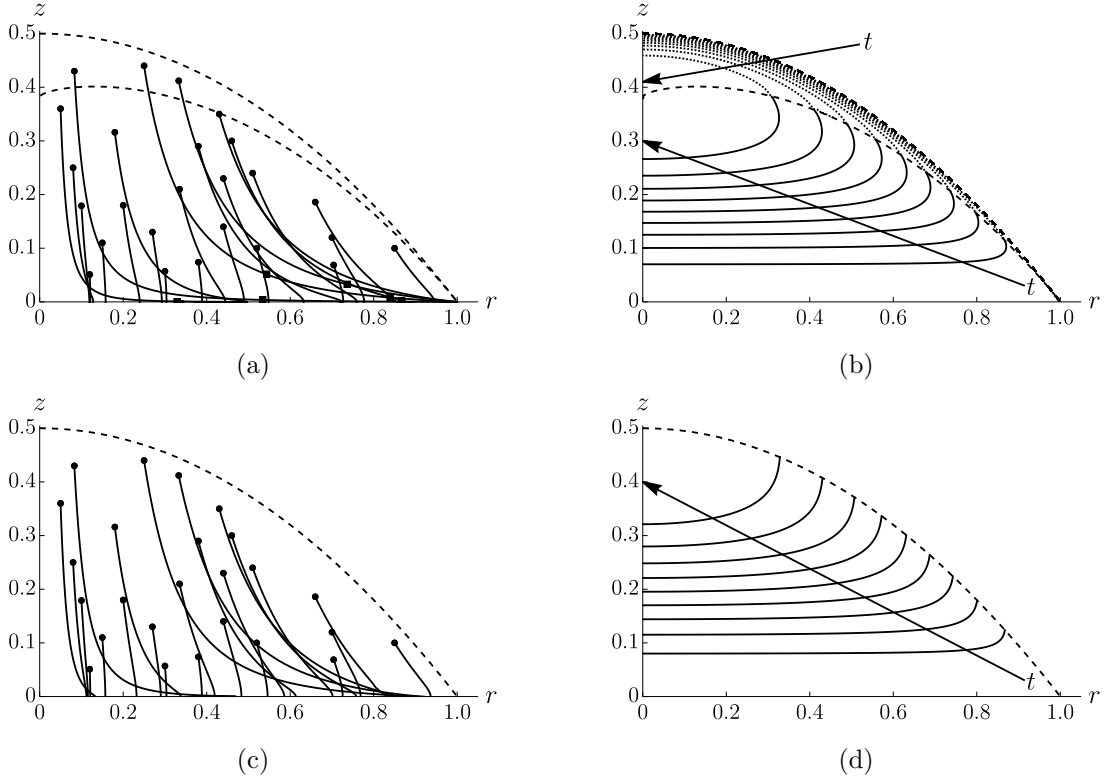


Figure 6.5: Plots of (a,c) the paths of a selection of representative particles and (b,d) the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) for a droplet evolving in the CR mode at $t = (1/10, 1/5, \dots, 9/10) \times t_{\text{CR}}$. In (a,c) the dots (•) denote the initial positions of the particles and the squares (■) denote the positions at which free-surface capture occurs. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dashed line in (c,d) indicates the critical watershed curve on which free-surface and substrate capture occur simultaneously, and the arrows in (b,d) indicate the directions of increasing t .

as discussed in Section 4.2.2.

6.3 A finitely thick, anisotropic, initially dry, porous substrate

6.3.1 Particle Paths in the CR Mode

The equations governing the paths of the particles within a droplet evolving in the CR mode are obtained by substituting the expression for u given by (4.61) and the

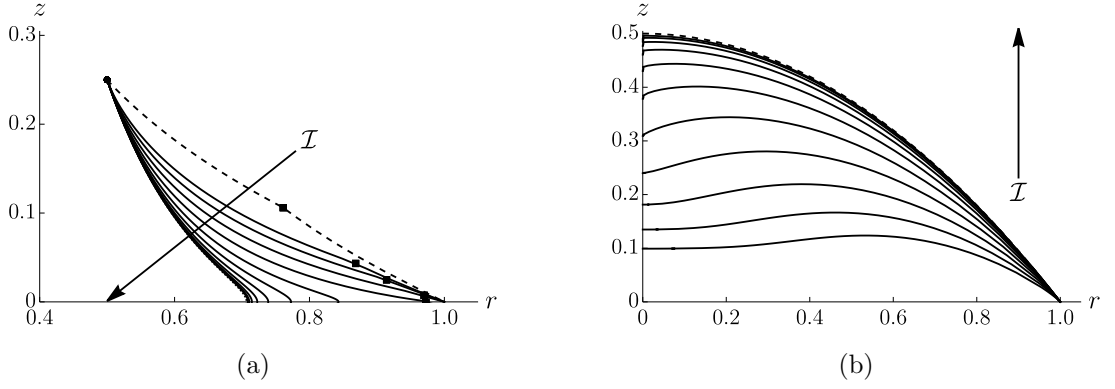


Figure 6.6: Plots of (a) the path of a representative particle for pure evaporation (dashed line), simultaneous evaporation and imbibition for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$ (solid lines), and pure imbibition (dotted line) and (b) the critical watershed curve within a droplet undergoing simultaneous evaporation and imbibition for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$ on a finitely thick, anisotropic, initially dry, porous substrate in the CR mode. The dots and squares in (a) represent the initial position and the point at which free-surface capture occurs, respectively, for each representative particle. The dashed line in (b) indicates the initial free-surface profile of the droplet $h(r, 0) = (1 - r^2)/2$.

expression for w given by (4.62) into (6.1) and (6.2), with J_I given by (2.57). Figure 6.5, which is analogous to Figure 6.1, but for a droplet evolving in the CR mode on a finitely thick, anisotropic, initially dry, porous substrate (with those of pure evaporation given by Figures 6.1(a,b)), shows that the paths of particles and the critical watershed curve exhibit qualitatively similar behaviour to that discussed in Section 6.2.1. Again, this behaviour is qualitatively different to that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$. Figure 6.6, which is analogous to Figure 6.2, but for a droplet evolving in the CR mode on a finitely thick, anisotropic, initially dry, porous substrate, shows that, in contrast to that discussed in Section 6.2.1, imbibition contributions dominate the flow at earlier times (i.e., as $t \rightarrow 0^+$), as discussed in Section 4.3.1.

6.3.2 Particle Paths in the CA Mode

The equations governing the paths of the particles within a droplet evolving in the CA mode are obtained by substituting the expression for u given by (4.76) and the expression for w given by (4.77) into (6.1) and (6.2), with J_I given by (2.57). Figure

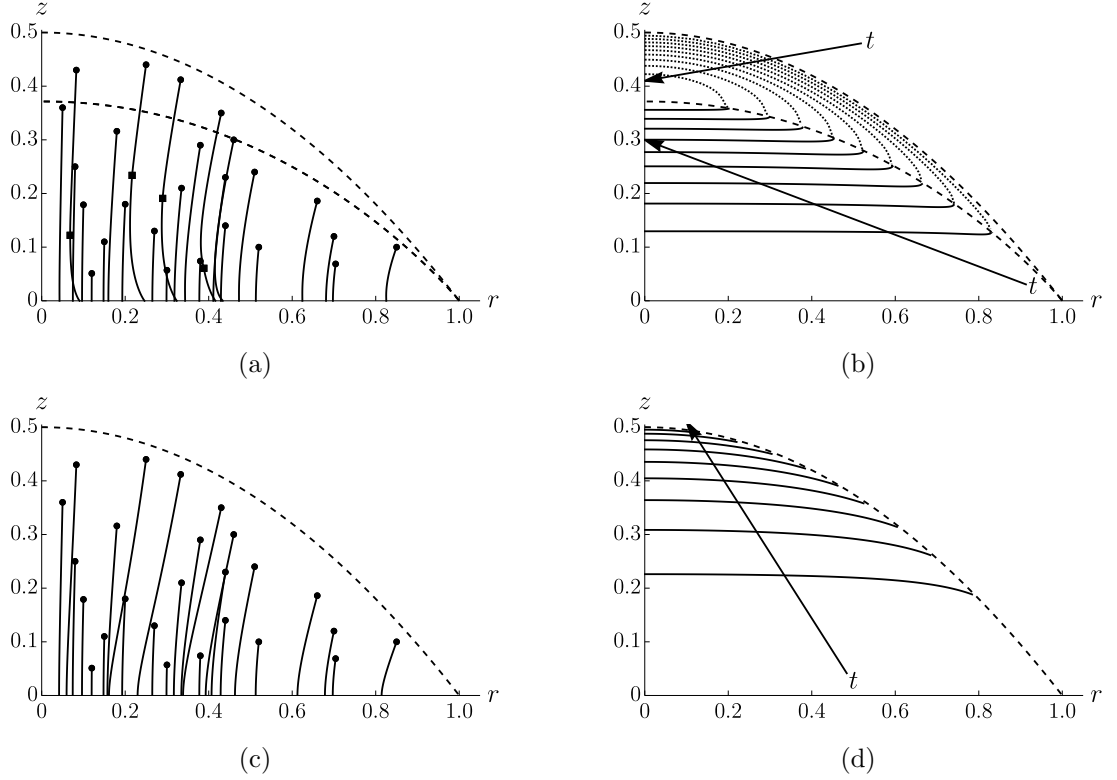


Figure 6.7: Plots of (a,c) the paths of a selection of representative particles and (b,d) the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) for a droplet evolving in the CA mode at $t = (1/10, 1/5, \dots, 9/10) \times t_{CA}$ for (a,b) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$, and (c,d) pure imbibition. In (a,c) the dots ($\bullet$) denote the initial positions of the particles, and in (a) the squares ($\blacksquare$) denote the positions at which free-surface capture occurs. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dashed line in (a,b) indicates the critical watershed curve on which free-surface and substrate capture occur simultaneously, and the arrows in (b,d) indicate the directions of increasing t .

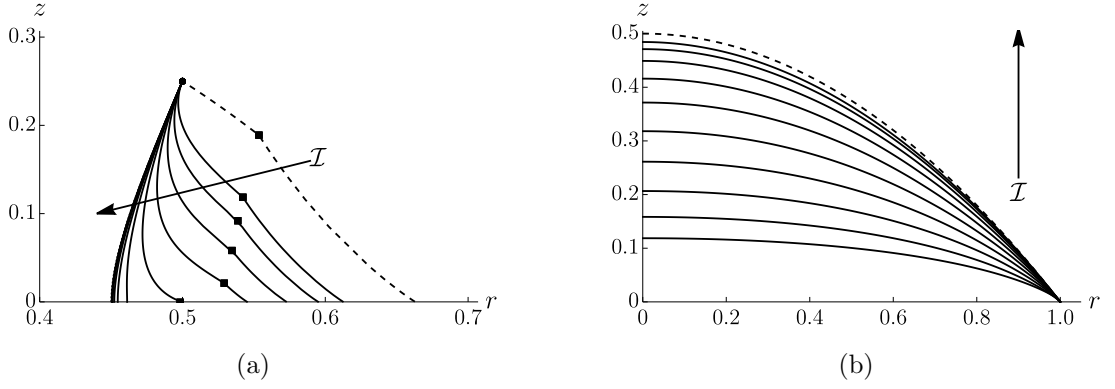


Figure 6.8: Plots of (a) the path of a representative particle for pure evaporation (dashed line), simultaneous evaporation and imbibition for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$ (solid lines), and pure imbibition (dotted line) and (b) the critical watershed curve within a droplet undergoing simultaneous evaporation and imbibition for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -5, -4, \dots, 5$ on a finitely thick, anisotropic, initially dry, porous substrate in the CA mode. The dots and squares in (a) represent the initial position and the point at which free-surface capture occurs, respectively, for each representative particle. The dashed line in (b) indicates the initial free-surface profile of the droplet $h(r, 0) = (1 - r^2)/2$.

6.7, which is analogous to Figure 6.5 but for a droplet evolving in the CA mode, shows that the particle paths are qualitatively different from those for a droplet evolving in the CR mode. In particular, Figure 6.7 illustrates that, in contrast to Sections 6.2.2 and 6.3.1, the particles experience radially inwards and outwards flow as the droplet evolves due to the interplay between evaporation and imbibition contributions to the flow, with imbibition contributions dominating at earlier times (i.e., as $t \rightarrow 0^+$), as discussed in Section 4.3.2. However, similarly to Section 6.2.2, the motion of the (unpinned) contact line means that the particles are always deposited as a distributed deposit within the initial footprint of the droplet, as sketched in Figure 2.7(b). This behaviour is qualitatively the same as that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$, as discussed in Sections 2.8 and 5.2. Figure 6.8, which is analogous to Figure 6.4, but for a droplet evolving in the CA mode on a finitely thick, anisotropic, initially dry, porous substrate, shows that, in contrast to that discussed in Section 6.2.2, imbibition contributions dominate the flow at earlier times (i.e., as $t \rightarrow 0^+$).

6.4 A finitely thick, anisotropic, flooded, porous substrate

6.4.1 Particle Paths in the CR Mode

The equations governing the paths of the particles within a droplet evolving in the CR mode are obtained by substituting the expression for u given by (4.61) and the expression for w given by (4.62) into (6.1) and (6.2), with J_I given by (2.65). Figure 6.9, which is analogous to Figures 6.1 and 6.5, but for a droplet evolving in the CR mode on a finitely thick, anisotropic, flooded, porous substrate (with those of pure evaporation given by Figures 6.1(a,b)), shows that the paths of particles and the critical watershed curve exhibit qualitatively similar behaviour to that discussed in Sections 6.2.1 and 6.3.1. We note that Figures 6.5(c) and 6.7(c) are identical as u/w , where u is given by (4.66) or (4.71) and w is given by (4.67) or (4.72), is independent of J_I . Again, this behaviour is qualitatively different to that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$. Figure 6.10, which is analogous to Figures 6.2 and 6.6, but for a droplet evolving in the CR mode on a finitely thick, anisotropic, flooded, porous substrate, shows that, similarly to that discussed in Section 6.2.1, evaporation contributions dominate the flow at later times (i.e., as $t \rightarrow t_{\text{CR}}^-$).

6.4.2 Particle Paths in the CA Mode

The equations governing the paths of the particles within a droplet evolving in the CA mode are obtained by substituting the expression for u given by (4.76) and the expression for w given by (4.77) into (6.1) and (6.2), with J_I given by (2.65). Figure 6.11, which is analogous to Figure 6.9 but for a droplet evolving in the CA mode, shows that the particle paths are qualitatively different than those for a droplet evolving in the CR mode. In particular, Figure 6.11 illustrates that, similarly to Section 6.3.2, the particles experience radially inwards and outwards flow as the droplet evolves due to the interplay between evaporation and imbibition contributions to the flow, with imbibition contributions dominating at later times (i.e., as $t \rightarrow t_{\text{CA}}^-$) as discussed in Section 4.3.2. However, similarly to Sections 6.2.2 and 6.3.2, the motion of the (unpinned) contact line means that the particles are always deposited as a distributed deposit within the

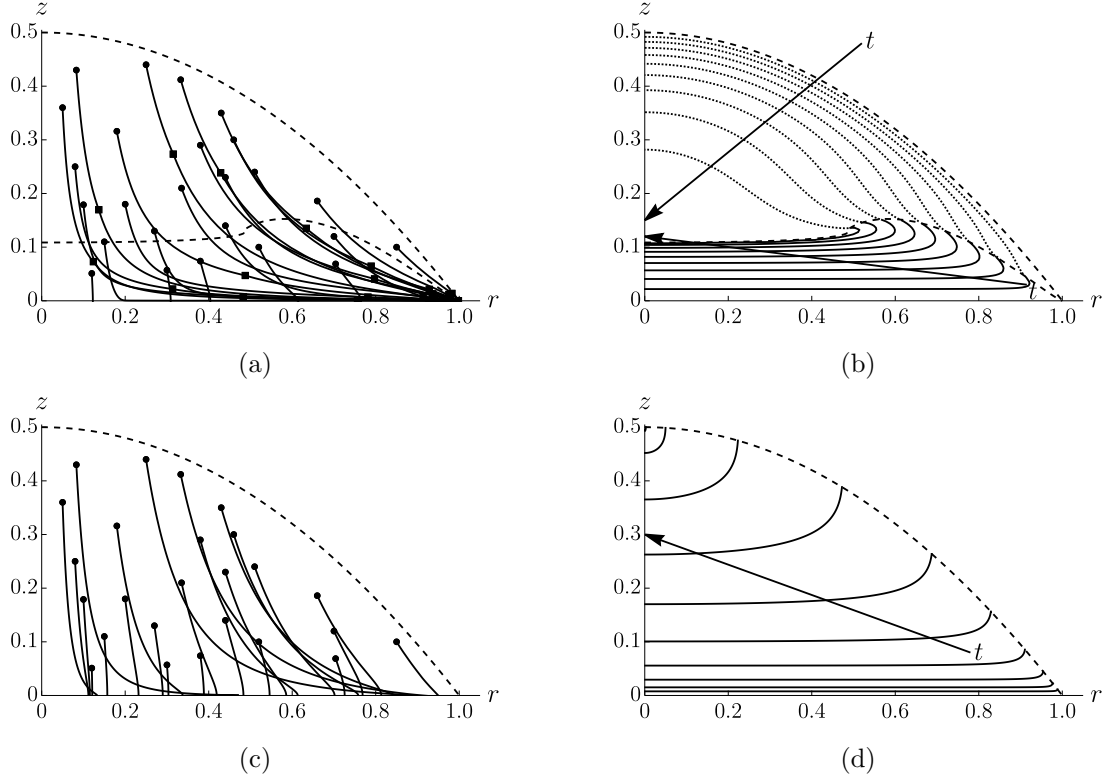


Figure 6.9: Plots of (a,c) the paths of a selection of representative particles and (b,d) the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) for a droplet evolving in the CR mode at $t = (1/10, 1/5, \dots, 9/10) \times t_{\text{CR}}$ for (a,b) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$, and at $t = 2^n \times 4$ ($n = -10, -9, \dots, 0$) for (c,d) pure imbibition. In (a,c) the dots ($\bullet$) denote the initial positions of the particles and the squares ($\blacksquare$) denote the positions at which free-surface capture occurs. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dashed line in (a,b) indicates the critical watershed curve on which free-surface and substrate capture occur simultaneously, and the arrows in (b,c) indicate the directions of increasing t .

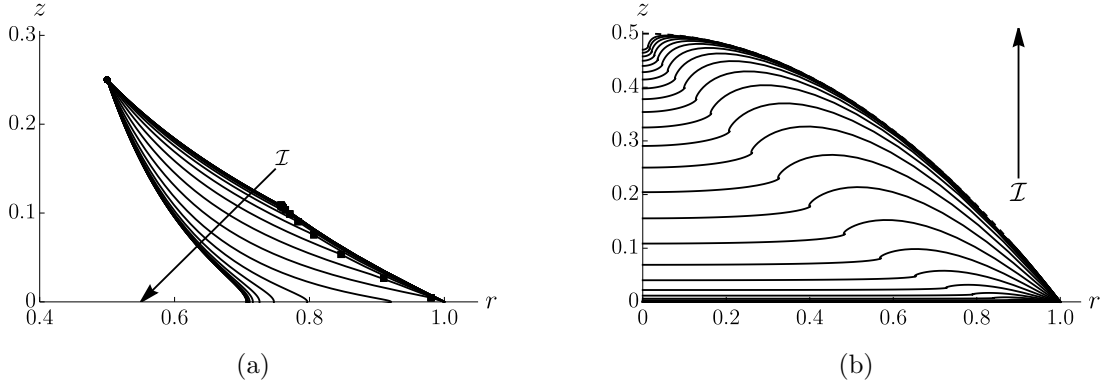


Figure 6.10: Plots of (a) the path of a representative particle and (b) the critical watershed curve for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -15, -14, \dots, 15$ within a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, initially dry, porous substrate in the CR mode. The dots and squares in (a) represent the initial position and the point at which free-surface capture occurs, respectively, for each representative particle. The dashed line in (b) indicates the initial free-surface profile of the droplet $h(r, 0) = (1 - r^2)/2$.

initial footprint of the droplet, as sketched in Figure 2.7(b). We note that Figures 6.7(c) and 6.9(c) are identical as u/w , where u is given by (4.80) or (4.85) and w is given by (4.81) or (4.86), is independent of J_1 . This behaviour is qualitatively the same as that in the regime $\hat{\theta}_0^2 \ll \text{Pe}^* \ll 1$, as discussed in Sections 2.8 and 5.2. Figure 6.12, which is analogous to Figure 6.10, but for a droplet evolving in the CA mode on a finitely thick, anisotropic, flooded, porous substrate, shows that, similarly to that discussed in Section 6.2.2, imbibition contributions dominate the flow at later times (i.e., as $t \rightarrow t_{\text{CR}}^-$).

6.5 Conclusions

In Chapter 6 we have analysed mathematical models for the transport and deposition of particles within the droplet and onto the substrate in the CR and CA modes in the alternative regime in which diffusion of particles is slower than both radial and axial advection of particles, and hence at leading order diffusion of particles plays no role and the transport of particles is purely advective. In particular, we determined the paths of particles within a droplet undergoing simultaneous evaporation and imbibition in the

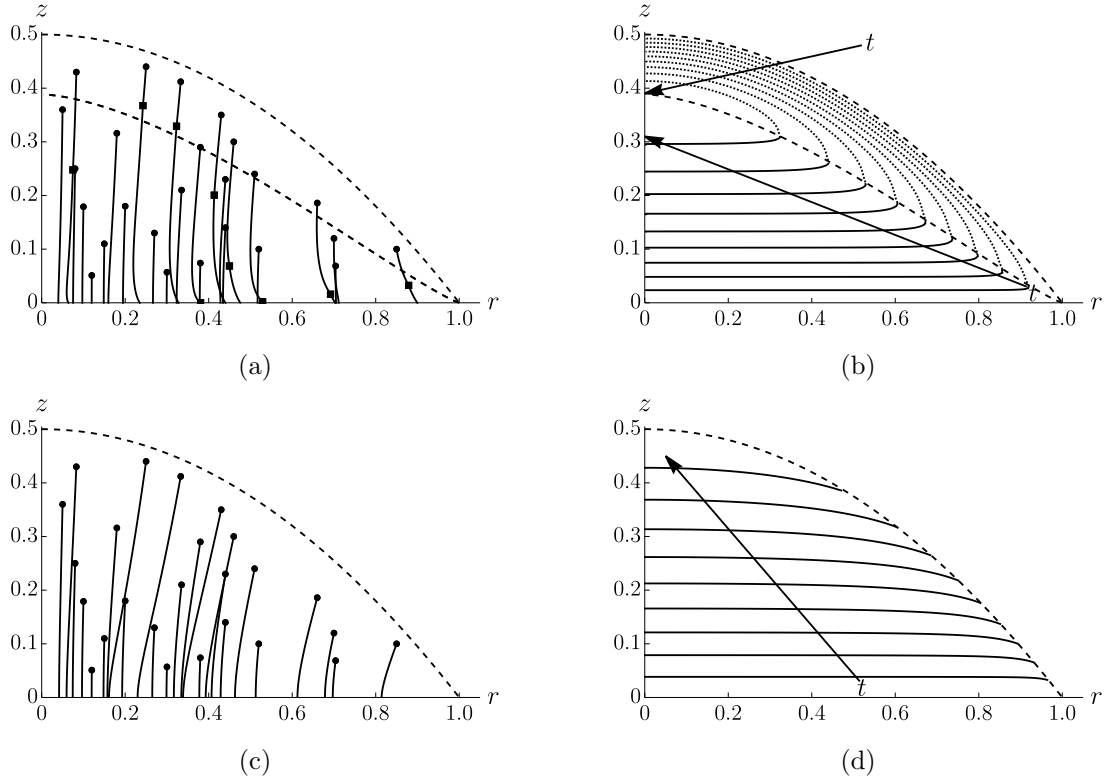


Figure 6.11: Plots of (a,c) the paths of a selection of representative particles and (b,d) the locus of the initial positions of particles that are captured by either the free surface (dotted lines) or the substrate (solid lines) for a droplet evolving in the CA mode at $t = (1/10, 1/5, \dots, 9/10) \times t_{CA}$ for (a,b) simultaneous evaporation and imbibition with $\mathcal{E} = \mathcal{I} = 1$, and (c,d) pure imbibition. In (a,c) the dots ($\bullet$) denote the initial positions of the particles, and in (a) the squares ($\blacksquare$) denote the positions at which free-surface capture occurs. The parabolic dashed line indicates the initial free-surface profile of the droplet, $h(r, 0) = (1 - r^2)/2$, the dashed line in (a,b) indicates the critical watershed curve on which free-surface and substrate capture occur simultaneously, and the arrows in (b,d) indicate the directions of increasing t .

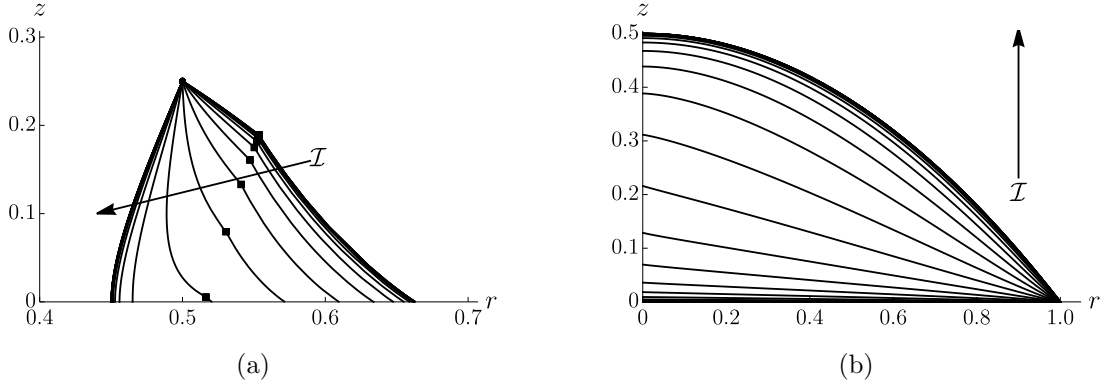


Figure 6.12: Plots of (a) the path of a representative particle and (b) the critical watershed curve for $\mathcal{E} = 1$ and $\mathcal{I} = 2^n$, $n = -15, -14, \dots, 15$ within a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, initially dry, porous substrate in the CA mode. The dots and squares in (a) represent the initial position and the point at which free-surface capture occurs, respectively, for each representative particle. The dashed line in (b) indicates the initial free-surface profile of the droplet $h(r, 0) = (1 - r^2)/2$.

CR and CA modes.

In Section 6.2 we determined the paths of particles within a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate in the CR and CA modes, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.1, respectively. We showed that the final deposit is a single ring for a droplet undergoing pure evaporation. In contrast, for a droplet undergoing simultaneous evaporation and imbibition the final deposit consists of a combination of a ring deposit and a distributed deposit, while for pure imbibition the deposit is a distributed deposit. These results are qualitatively different from the regime discussed in Chapter 5 for simultaneous evaporation and imbibition and for pure imbibition, respectively. We also showed that in the CA mode a distributed deposit is formed for a droplet undergoing pure evaporation, simultaneous evaporation and imbibition, and pure imbibition, respectively. These results are qualitatively different from those discussed in Chapter 5.

In Section 6.3 we determined the paths of particles within a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, initially dry, porous substrate in the CR and CA modes, where the evaporation and imbibition

problems are described in Sections 2.6 and 2.7.2, respectively. We again showed that in the CR mode for a droplet undergoing simultaneous evaporation and imbibition the final deposit is a combination of a ring deposit and a distributed deposit, whereas for pure imbibition the final deposit is a distributed deposit. We also showed that in the CA mode a distributed deposit is formed for a droplet undergoing simultaneous evaporation and imbibition and for pure imbibition, respectively. The findings in Section 6.3 are qualitatively similar to those in Section 6.2.

In Section 6.4 we determined the paths of particles within a droplet undergoing simultaneous evaporation and imbibition on a finitely thick, anisotropic, flooded, porous substrate in the CR and CA modes, where the evaporation and imbibition problems are described in Sections 2.6 and 2.7.3, respectively. We again showed that in the CR mode for a droplet undergoing simultaneous evaporation and imbibition the final deposit is a combination of a ring deposit and a distributed deposit, whereas for pure imbibition the final deposit is a distributed deposit. We also showed that in the CA a distributed deposit is formed for a droplet undergoing simultaneous evaporation and imbibition and for pure imbibition, respectively. The findings in Section 6.4 are qualitatively similar to those in Sections 6.2 and 6.3.

The results described in Chapter 6 indicate that, in contrast to the results described in Chapter 5, in the alternative regime (i.e., $Pe^* \gg 1$) evaporation and imbibition have a qualitatively different effect on the transport of particles in the CR mode, with the evolution towards the ring deposit and distributed deposit based on the relative strength of evaporation and/or imbibition, respectively. We have also demonstrated that the quantitative differences in the local imbibition mass flux, as described in Sections 2.7.1, 2.7.2, and 2.7.3, lead to similar distributed deposits in the CR and CA modes, however, the time at, and mechanism of capture in, which particles are deposited onto the surface of the substrate differs for each local imbibition mass flux, respectively. In Chapter 7, we will discuss potential directions of further work to quantify the nature of the final deposit in this alternative regime for the three situations discussed in Sections 6.2, 6.3, and 6.4, respectively, in the CR and CA modes, as well as further work and conclusions for the mathematical models and subsequent results developed throughout this thesis.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

Throughout this thesis we have developed and analysed mathematical models that describe the evolution of, flow within, and deposition of particles from, a thin particle-laden sessile droplet undergoing simultaneous evaporation and imbibition on three porous substrates, namely an infinitely thick, isotropic, flooded, porous substrate, a finitely thick, anisotropic, initially dry, porous substrate, and a finitely thick, anisotropic, flooded, porous substrate. Motivated by the fact that evaporation and imbibition have largely been studied separately, the work presented within this thesis provides a description of their combined influence on the evolution of, flow within, and deposition of particles from a thin particle-laden sessile droplet. Overall, this thesis provides the first comprehensive lubrication-theory based framework that considers evaporation, imbibition, droplet evolution, flow within the droplet and the substrate, and particle transport in multiple modes of evolution, porous substrates, and particle transport regimes.

In Chapter 2, we formulated a mathematical model for a thin, particle-laden, sessile droplet undergoing simultaneous evaporation and imbibition on a porous substrate. The governing equations for the droplet geometry, flow within the droplet, and global mass balance were derived using a lubrication-theory based approach, together with the corresponding boundary conditions at the free surface, contact line, and solid-liquid interface, respectively. The chapter also introduced the porous substrate models used

in the remainder of this thesis, namely an infinitely thick, isotropic, flooded, porous substrate, finitely thick, anisotropic, dry and flooded, porous substrate. Furthermore, we formulated a mathematical model for the particle transport and deposition problem. The model formulated in Chapter 2 provides the foundation for the subsequent analysis of droplet evolution, flow within the droplet and the substrate, and particle transport in Chapters 3–6.

In Chapter 3, we determined the evolution, and hence the lifetime, of a thin sessile droplet in the CR, CA, SS, and SJ modes on the three porous substrates considered in this thesis. For an infinitely thick, isotropic, flooded substrate, we identified contrasting behaviours between pure evaporation and pure imbibition, including the infinite lifetime associated with pure imbibition in the CR mode and the non-monotonic dependence of the SS and SJ lifetimes on the critical angle and de-pinning angle, respectively (i.e., θ^* and $\theta_{\min}$). For a finitely thick, anisotropic, initially dry substrate, all modes exhibit finite lifetimes, the SS and SJ lifetimes are monotonic, and the evolution, and hence the final depth, of the wetting front were characterised for each mode, respectively. For a finitely thick, anisotropic, flooded substrate, scaling laws for the CA mode were identified, with the “ d^2 law” being true regardless of the relative strengths of evaporation and/or imbibition. Together, these results provide a comprehensive description of droplet evolution on three different porous substrates and highlight the need for further experimental verification and validation of such models.

In Chapter 4, we determined the flow within the droplet and the substrate in the CR, CA, SS, and SJ modes, for the three porous substrates considered in this thesis. Building on previous work on evaporating droplets on non-porous substrates, we showed that the flow within the droplet is the sum of the evaporation and imbibition contributions. For an infinitely thick, isotropic, flooded substrate the flow is always directed outwards and downwards, while for finitely thick, anisotropic substrates with a spatially uniform local imbibition mass flux the flow exhibits qualitatively different behaviour across the modes, including regions of inwards, outward, and zero flow in the CA mode. Furthermore, the behaviour of the flow within the droplet and the substrate in the CR and CA phases of the SS mode and the n th CR phase of the SJ mode are

qualitatively similar those in the CR and CA mode, and the CR mode, respectively. Furthermore, these results provide analytical expressions that can be directly compared with experimental measurements.

In Chapter 5, we determined the transport and deposition of particles in the regime where diffusion is faster than axial advection but slower than radial advection (i.e., $Pe^* \ll 1$). For an infinitely thick, isotropic, flooded, porous substrate we showed that the final deposit pattern in each mode (i.e., a ring deposit, a distributed deposit, a combined ring and distributed deposit, and multiple ring deposits, as sketched in Figure 2.7) is, perhaps unexpectedly, independent of the mechanism driving mass loss, with the nature of the distributed deposit taking the form of a cleaved near-uniform deposit in the CA and SS modes. For finitely thick, anisotropic substrates, the final deposit in the CA modes depends on both the nature and strength of evaporation and imbibition, and encompass a wide range of final deposit patterns, including cleaved near-uniform, uniform, volcano, dome, and peak final deposit patterns. Furthermore, we demonstrated that evaporation and imbibition have the same qualitative effect on particle transport in the CR mode, while quantitative differences in the local imbibition mass flux determine the nature of the final deposit pattern in the CA mode. These results provide a clear framework for understanding how substrate properties and mass loss mechanisms determine the nature of the final deposit pattern and offer further routes for experimental verification and validation of the results described in this thesis.

In Chapter 6, we determined the transport of particles in the regime where diffusion is slower than both radial and axial advection, so that particle transport is purely advective at leading order. We calculated the particle paths in the CR and CA modes for droplets undergoing pure evaporation, pure imbibition, and simultaneous evaporation and imbibition on the three porous substrates considered in this thesis. Specifically, we showed that pure evaporation produces a single ring in the CR mode, pure imbibition produces a distributed deposit, and simultaneous evaporation and imbibition produces a combination of the two, whilst, in the CA mode all situations led to a distributed deposit. These results are in contrast with those of Chapter 5, demonstrating that evaporation and imbibition have a qualitatively different influence on particle transport in

the advection-dominated regime, with the final deposit in the CR mode determined by the relative strength of evaporation and imbibition. Although the distributed deposits in the CR and CA modes are similar for the different local imbibition mass fluxes considered, the time at which particles are captured differs. These findings provide an enhanced understanding of deposition in both regimes and motivate further work on quantifying final deposit patterns in this regime: a preliminary analysis of such deposits is discussed in Section 7.2.

Overall, the results presented in this thesis advance the understanding of evaporating and imbibing droplets, clarify the influence of evaporation and imbibition on particle deposition, and establish a lubricated theory modelling framework that can be modified to incorporate additional physical processes (such as, multiple droplets, particle interactions, and multicomponent droplets). The final section outlines several opportunities for future work, including extensions to porous substrate modelling, further analyses of particle transport, and the incorporation of particle interactions. These directions highlight the breadth of possible extensions and underscore the potential for continued progress in understanding the complex interplay between evaporation, imbibition, and particle deposition; processes that remain central to both fundamental understanding and practical applications in a wide variety of contexts.

7.2 Future Work

Whilst the present work offers new insight into the simultaneous effects of evaporation and imbibition on particle transport, several aspects of the problem remain open to further study. In particular, the behaviour of multiple droplets evaporating and/or imbibing on porous substrates, the evolution of non-thin droplets or droplets with non-circular footprints, and situations in which the effect of gravity is not negligible all present natural extensions of the analysis performed in this thesis. These examples illustrate the breadth of possible future directions, and the remainder of this section outlines several further opportunities for extending the present work.

7.2.1 Extensions to the Droplet Modelling

The lubrication-theory based approach used throughout this thesis is asymptotically valid in the limit of small contact angles, although, as demonstrated in numerous studies of evaporating droplets, thin-film models often remain accurate beyond their formal range of validity (see, for example, Deegan [52], Hu & Larson [59], Wray *et al.* [71], and Larsson & Kumar [111]). Nevertheless, extending the analysis presented within this thesis to consider droplets with larger contact angles would be a natural direction for future work. Such an extension would require replacing the thin-film approximation with a more sophisticated modelling approach or direct numerical simulation of the full Navier–Stokes equation. Furthermore, the current analysis within this thesis could be extended to consider multicomponent (or multisolvent) droplets and, hence, the influence of solutal Marangoni flows on particle transport (see, for example, Rocha *et al.* [214,239]). This would be particularly relevant in the context of ink droplets, which often consist of complex liquid mixtures and suspended particles (see, for example, Lohse [168]).

7.2.2 Extensions to the Porous Substrate Modelling

The porous substrate models developed in Chapter 2 focus on idealised geometries, including an infinitely thick, isotropic, flooded, porous substrate and a finitely thick, anisotropic, dry or flooded, porous substrate. While these models capture the essential physics of imbibition, several generalisations merit further investigation. Firstly, the model for imbibition on an infinitely thick, flooded substrate could be extended to consider multiple droplets undergoing competitive imbibition. Analogous to the competitive evaporation of multiple thin sessile droplets (see, for example, Wray *et al.* [71,72] and Iqtidar *et al.* [240]), neighbouring droplets on a porous substrate may compete for pore space and one could reasonably expect similar competitive effects for evaporating and/or imbibing droplets. Such an extension would be particularly relevant to applications which include arrays of droplets in close proximity (such as printing, coating, and additive manufacturing). Secondly, the present models do not

account for substrate deformation or swelling. Extending the analysis to deformable or swellable porous substrates (such as hydrogels, polymer networks, or biological tissues) would require coupling Darcy flow with poro-elastic or multiphase mechanics (see, for example, Anderson [138] and Boulogne *et al.* [154]). Furthermore, extending the model developed for a finitely thick, anisotropic, initially dry, porous substrate to also consider flow in the radial direction (and, hence, make the substrate isotropic) may offer insight into the inner (on the surface) and outer (within the substrate) ring experimentally investigated by Li *et al.* [6], and shown in Figure 1.8.

7.2.3 Extensions to the Particle Transport Modelling

Particle–substrate adsorption effects may play a significant role across a variety of applications and situations, as discussed in Section 1.8.4. We will briefly summarise some preliminary work that describes the deposit in CR mode in the presence of particle–substrate adsorption. Building on the works of Zigelman & Manor [176], D’Ambrosio *et al.* [83], and Moore *et al.* [184] who considered the effect of particle–substrate adsorption on a droplet undergoing pure evaporation in the CR mode, we consider the effect of particle–substrate adsorption on the transport and deposition of particles from a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate in the CR mode. Following the approach of D’Ambrosio *et al.* [83], we find that ϕ is given by

$$\phi = \frac{s}{\theta^{1/4}s_0} \left[\frac{(1-s)^2(1+s_0+s_0^2)}{(1-s_0)^2(1+s+s^2)} \right]^{\pi\text{Da}/[12(\mathcal{E}+2\mathcal{I}\theta)]} \times \exp \left[\frac{\pi\text{Da}}{2(3)^{1/2}(\mathcal{E}+2\mathcal{I}\theta)} \arctan \left(\frac{(3)^{1/2}(s_0-s)}{2+s_0+s+2s_0s} \right) \right], \quad (7.1)$$

where $s = s(r, t)$ is given by

$$s = \theta^{1/4} \left[\theta^{-3/4} - 1 + (1-r^2)^{3/2} \right]^{1/3}, \quad (7.2)$$

$s_0 = s(r, 0) = (1-r^2)^{1/2}$, and Da ($= O(1)$) is the appropriately defined Damköhler number that characterises the ratio of particle–substrate adsorption and advective

timescales (see, for example, Zigelman & Manor [176], D'Ambrosio *et al.* [83], and Moore *et al.* [184]), Setting $Da = 0$ in (7.1) recovers the solution for ϕ in the absence of particle–substrate adsorption given by equation (5.10). Similarly, the solution for ϕ for a droplet undergoing pure evaporation and pure imbibition are recovered in the respective limits.

The density of particles adsorbed onto the surface of the substrate, denoted by $\phi_{\text{ads}} = \phi_{\text{ads}}(r, t)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0 \hat{\phi}_{\text{ref}}$, is given by

$$\phi_{\text{ads}} = Da \int_0^t \phi(r, t) r \, dt \quad \text{for } 0 \leq r \leq 1, \quad (7.3)$$

and the mass of particles on the surface of the substrate, denoted by $M_{\text{ads}} = M_{\text{ads}}(t)$ and non-dimensionalised by $\hat{\theta}_0 \hat{R}_0^3 \hat{\phi}_{\text{ref}}$, is given by

$$M_{\text{ads}} = 2\pi \int_0^1 \phi_{\text{ads}} r \, dr. \quad (7.4)$$

We note that ϕ_{ads} , M_{drop} , M_{ring} , and M_{ads} must be determined numerically, which we implemented using the Mathematica [238] routine `NIntegrate[]`. Figures 7.1(a,b,c) show the evolutions of M_{drop}/M_0 , M_{ring}/M_0 , M_{ads}/M_0 , respectively, plotted as functions of t/t_{CR} for simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) on an infinitely thick, isotropic, flooded, porous substrate for a range of value of Da . Figure 7.1(d) shows $M_{\text{ads}}(t_{\text{CR}})/M_0$ plotted as a function of Da for $\mathcal{E} = 1$ and $\mathcal{I} = 2^{-15}$ (dashed line), $\mathcal{E} = \mathcal{I} = 1$ (solid line), and $\mathcal{E} = 2^{-15}$ and $\mathcal{I} = 1$ (dotted line). In particular, Figure 7.1 illustrates that, as in the situation of a droplet undergoing pure evaporation in the CR mode in the presence of particle–substrate adsorption, all of the particles initially within the droplet are eventually transferred to either the ring deposit at $r = 1$ or the distributed deposit in $0 \leq r < 1$. We note that a similar analysis could be performed for the CA, SS, and SJ modes, as well as for other porous substrates, such as a finitely thick, anisotropic, dry or flooded, porous substrate.

Building on the results in Chapter 6, we show results from preliminary investigation of the final deposit pattern in the advection-dominated regime by calculating the density of particles distributed on the surface of the substrate, denoted by $\phi_{\text{dist},N} = \phi_{\text{dist},N}(r)$,

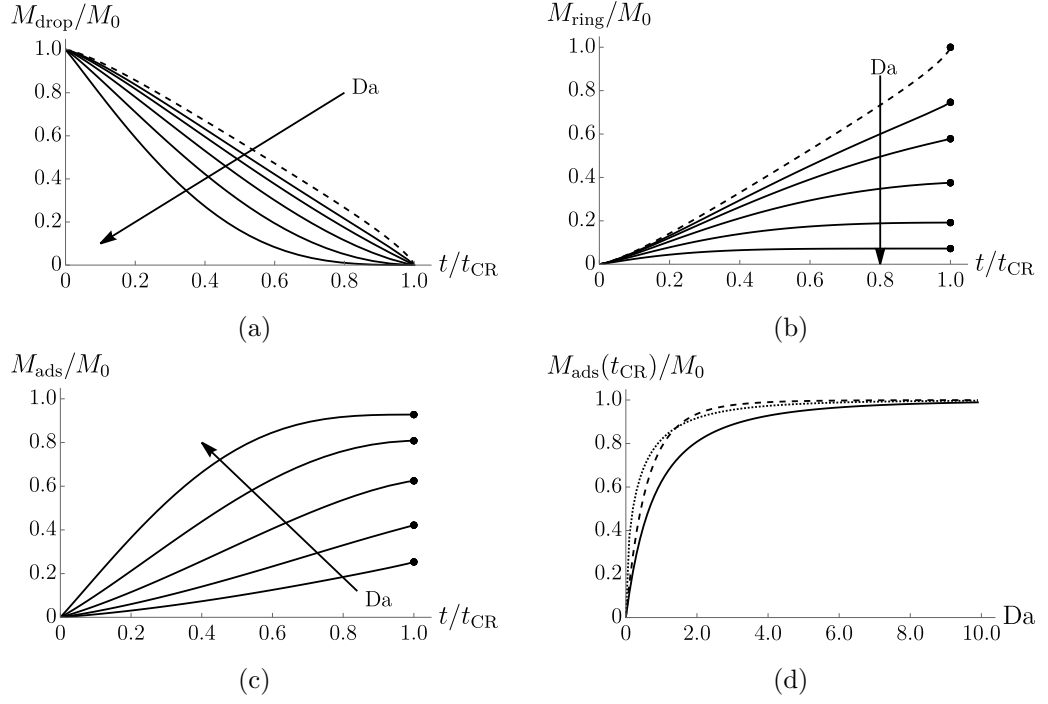


Figure 7.1: The evolutions of (a) M_{drop}/M_0 , (b) M_{ring}/M_0 , and (c) M_{ads}/M_0 in the CR mode plotted as functions of t/t_{CR} for simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate for $\mathcal{E} = \mathcal{I} = 1$ and $Da = 2^n$, $n = -2, -1, \dots, 2$. The dots in (b,c) denote the values of $M_{\text{ring}}(t_{\text{CR}})/M_0$ and $M_{\text{ads}}(t_{\text{CR}})/M_0$, respectively. (d) $M_{\text{ads}}(t_{\text{CR}})/M_0 (= 1 - M_{\text{ring}}(t_{\text{CR}})/M_0)$ in the CR mode plotted as functions of Da for simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate for $\mathcal{E} = 1$ and $\mathcal{I} = 2^{-15}$ (dashed line), $\mathcal{E} = \mathcal{I} = 1$ (solid line), and $\mathcal{E} = 2^{-15}$ and $\mathcal{I} = 1$ (dotted line). The dashed lines in (a,b) indicate the solutions for M_{drop}/M_0 and M_{ring}/M_0 in the absence of particle–substrate adsorption (i.e., $Da = 0$) given by (5.12) and (5.13), respectively.

in both the CR and CA modes for a droplet undergoing simultaneous evaporation and imbibition on an infinitely thick, isotropic, flooded, porous substrate. A uniformly spaced grid of 8×10^4 points (i.e., initial particles) is generated in the region $0 < r < 1$ and $0 < z < 0.5$. From this set, we retain only those points within region bounded by the initial free surface of the droplet (53,470 points) or, in the simultaneous evaporation and imbibition problem in the CR mode, those located within the region bounded by the watershed curve (16,350 points). In the CA mode, all particles are transported to a distributed deposit, so the number of points is always 53,470 points. Each particle is then advected to its final position, and $\phi_{\text{dist},N}$ is calculated by fitting a normalisation constant. Specifically, when all particles are transported to the distributed deposit, the total mass is taken to be $M_0 = \pi/4$; when only particles bounded by the critical watershed curve contribute, the total mass is obtained by integrating the bounded region over the droplet footprint. This ensures that the values of $\phi_{\text{dist},N}$ are consistent across both regions and can be compared quantitatively. We note that, similarly to ϕ_{dist} , $\phi_{\text{dist},N}$ does not capture particles that are transported to the contact line. To calculate $\phi_{\text{dist},N}$, the final particle positions are binned into 100 uniformly spaced intervals over $0 < r < 1$, with particles whose final positions lie between $r = 0$ and $r = 0.01$ grouped into the bin centred at $r = 0.005$, and so on.

Figure 7.2(a) shows $\phi_{\text{dist},N}$ plotted as a function of r in the CR mode for simultaneous evaporation and imbibition (solid line) and pure imbibition (dotted line). In particular, Figure 7.2(a) illustrates that, as expected, fewer particles are distributed onto the surface of the substrate for the simultaneous evaporation and imbibition problem than that of pure imbibition, and that $\phi_{\text{dist},N}$ increases as $r \rightarrow 1^-$, consistent with the flow always being outwards. Figure 7.2(b) shows $\phi_{\text{dist},N}$ plotted as a function of r in the CA mode for pure evaporation (dashed line), simultaneous evaporation and imbibition (solid line), and pure imbibition (dotted line). In particular, Figure 7.2(b) illustrates that $\phi_{\text{dist},N}$ is qualitatively similar for pure evaporation, simultaneous evaporation and imbibition, and pure imbibition, and that the nature of the final deposit pattern resembles that of a dome deposit type, as sketched in Figure 1.7(h).

As with any numerical evaluation of this nature, the smoothness of $\phi_{\text{dist},N}$ is limited

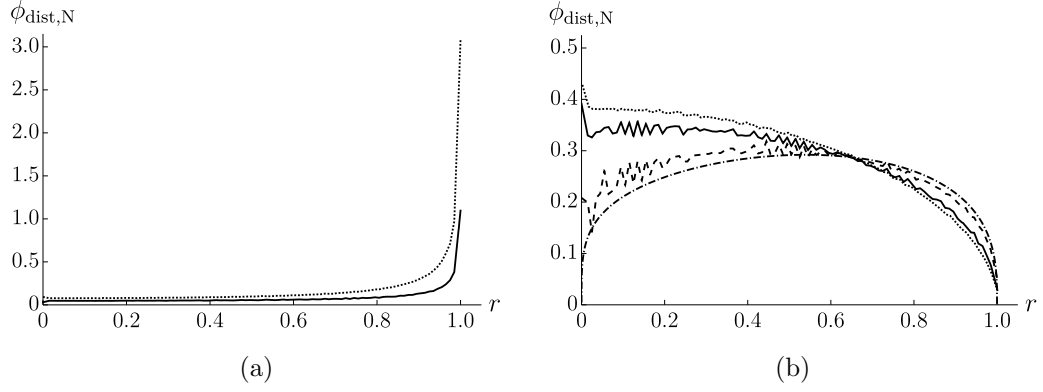


Figure 7.2: $\phi_{\text{dist},N}$ in the regime $\text{Pe}^* \gg 1$ for (a) the CR mode for simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) (solid line) and pure imbibition (dotted line) and (b) the CA mode for pure evaporation (dashed line), simultaneous evaporation and imbibition ($\mathcal{E} = \mathcal{I} = 1$) (solid line) and pure imbibition (dotted line). The dashed-dotted line in (b) indicates the solution for ϕ_{dist} given by (5.26) in the regime $\text{Pe}^* \ll 1$.

by the number of sampled points. If a larger number of points were used, we would expect the residual noise in $\phi_{\text{dist},N}$ to diminish and the corresponding distribution to become smoother. Moreover, the behaviour of $\phi_{\text{dist},N}$ depends not only on the number of sampled points but also on the binning scheme, such as whether the bin widths are uniform or varying. Preliminary analysis shows that increasing the number of bins enhances the resolution but also amplifies residual noise, while using fewer bins suppresses noise at the cost of detail. These considerations must be taken into account when interpreting the results obtained and, hence, such results should be regarded as more qualitative than quantitative descriptions of the nature of the final deposit pattern.

Additionally, many practical systems involve particles that are anisotropic or non-uniform in size. Such particles experience strong, long-range particle–particle attractive interactions and the final deposit pattern does not coincide with those predicted by the models presented in Chapters 5 and 6 (see, for example, the experimental investigation of Yunker *et al.* [9]). Finally, a further direction concerns droplets containing biological or active particles, which introduce several additional mechanisms that are absent from the neutrally-buoyant and hydrodynamically passive particles considered in this thesis (see, for example, Carreón *et al.* [163] and Wilting *et al.* [241]).

Chapter 7. Conclusions and Future Work

In conclusion, the modelling, results, and analysis presented in this thesis establish a comprehensive lubrication-theory based mathematical framework for understanding the behaviour of a thin particle-laden droplet undergoing simultaneous evaporation and imbibition on a porous substrate, whilst also identifying several directions for future investigations.

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