Flow of thin liquid films on chemically structured substrates

MARKUS RAUSCHER and S. DIETRICH
Max-Planck-Institut für Metallforschung,
Heisenbergstr. 3, 70569 Stuttgart, Germany, and
Institut für Theoretische und Angewandte Physik,
Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany

(March 22, 2022)

Abstract

Chemically patterned surfaces are of significant interest in the context of microfluidic applications. Miniaturization of such devices will eventually lead to structures on the nano-scale. Whereas on the micron scale purely macroscopic descriptions of liquid flow are valid, on the nanometer scale long-ranged inter-molecular interactions, thermal fluctuations such as capillary waves, and finally the molecular structure of the liquid become important. We discuss the most important conceptual differences between flow on chemically patterned substrates on the micron scale and on the nanometer scale. These concern the structure of the triple line, the type of interactions between neighboring liquid flows, and the influence of the molecular structure of the liquid on the flow. We formulate four design issues for nanofluidics related to channel width, channel separation, and channel bending radius, and conclude with a discussion of the relevance of the conceptual differences between the micron scale and the nanometer scale for these issues.

1 Introduction

In recent years substantial efforts have been invested in miniaturizing chemical processes by building microfluidic systems. The “lab on a chip concept” integrates a great variety of chemical and physical processes into a single device [14, 24, 27] in a similar way as an integrated circuit incorporates many electronic devices into a single chip. These microfluidic devices do not only allow for cheap mass production but they can operate with much smaller quantities of reactants and reaction products than standard laboratory equipments. This is particularly important for rare and expensive substances such as certain biological substances and for toxic or explosive materials. Even though most available microfluidic devices today have micron sized channels further miniaturization is leading towards
Figure 1: Schematic picture of liquid flow guided by so-called chemical walls on a chemically patterned substrate. The liquid moves along lyophilic stripes (light grey) on a lyophobic substrate (dark grey). The liquid layer ends in a three-phase contact line and a liquid monolayer (the precursor film) spreads ahead of it.

the nano-scale. Besides meeting technical challenges, new theoretical concepts are needed to understand the basic physical processes underlying this new technology. Whereas the ultimate limits for the miniaturization of electronic devices are set by quantum fluctuations, in a chemical chip these limits are determined by thermal fluctuations and can be explored by methods of classical statistical mechanics.

There are two main lines of development for microfluidic systems. The first one encompasses systems with closed channels. A common technique to produce these devices is to cast poly(dimethylsiloxane) (PDMS) over a topographically structured master, to peel off the polymer after curing, and to seal the resulting topographically structured material onto a flat surface. This way rather complicated devices including valves and pumps have been fabricated [16]. However, closed channel systems have the disadvantage that they can be easily clogged by solute particles such as colloids or large bio-polymers.

The second type of systems are open with a free liquid-vapor interface and the fluid is not confined by physical but by chemical walls. The idea is that the liquid will be guided by lyophilic stripes on an otherwise lyophobic substrate. There are two sub-types of this technique: using a single chemically patterned substrate [8, 12] (see also Fig. 1) or a chemically patterned slit pore [15, 21, 29], respectively. The substrate surfaces can be structured chemically by printing or photographic techniques. All the techniques are confined to two dimensions.

Liquids in contact with chemically structured substrates are not only of technological use but also enjoy high interest in basic research. Wetting on chemically structured substrates has been studied extensively on all length scales. For example adsorption on stripe patterns shows a rich morphology on the macro-scale [22, 3] as well as on the nano-scale [10, 4]. In this context flow of liquids has also been studied to a large extend. Most of this research has been focused on homogeneous substrates, in
particular on dynamic contact angles, dewetting of thin films, and flow of thin films in many circumstances. For a review see Ref. 25.

In the following we first describe briefly those equilibrium features of wetting on chemically patterned substrates which are most relevant for microfluidic applications. After discussing the characteristics of thin film flow on homogeneous substrates, we state the three main conceptual differences between micro-scale and nano-scale fluid transport in chemical channels. We conclude with formulating four design principles for nanofluidic devices.

2 Wetting on chemically patterned substrates

Equilibrium wetting phenomena on chemically patterned substrates have been analyzed theoretically in great detail on both the macroscopic and the microscopic scale. Microscopic theories, such as the successful density functional theory, take into account the finite range of inter-molecular attractions and short-ranged repulsions explicitly [11]. Density functional theories do not only allow to study the order of wetting transitions and the equilibrium shape of the wetting film but also the detailed microscopic structure of the liquid in the vicinity of the substrate and at the liquid-vapor interface [9].

In macroscopic theories, however, the inter-molecular interactions are approximated by local descriptions. For a wetting film this means that the free energy of the film is described by a bulk term proportional to the volume of the fluid, a surface tension term proportional to the area of the liquid-vapor interface, an interface term proportional to the area of the liquid-substrate interface, and a line tension term proportional to the length of the three phase contact line between liquid, vapor, and substrate. In most studies the line tension term is neglected. Macroscopic theories have been used to describe the shape of droplets on homogeneous and structured substrates [22, 6]. The equilibrium droplet shape in chemically patterned slit-like pores has also been studied with the same technique [28].

It is a great challenge to describe the intermediate scale between the microscopic and the macroscopic one. In most cases it is impossible to obtain analytical results from microscopic theories and numerical calculations are prohibitive for large systems. Current research focuses on extending the scope of macroscopic theories down to the meso-scale by incorporating microscopic effects such as the wave-length dependence of the surface tension [23] and detailed properties of the three phase contact line [1].

3 Flow of thin liquid films

Flow of thin liquid films on homogeneous substrates has been studied extensively, in particular the motion of the three-phase contact line, dewetting of thin films, the stability of falling liquid films, and Marangoni flow.
Apart from a few molecular dynamics simulations, in most studies the liquid flow is described in terms of meso-scale hydrodynamics. This means that the hydrodynamic equations are augmented with long-ranged liquid-substrate interactions and hydrodynamic slip of the liquid at the substrate (with slip lengths on the nanometer scale). For a review see Ref. [25]. In a phase-field description even compressibility effects and the finite width of the liquid-vapor interface have been taken into account [26]. The finite interface width in the phase field models is the only signature of thermal fluctuations taken into account in hydrodynamic thin film models up to now.

The main analytic tool in this approach is the so-called lubrication approximation, which is a small-gradient expansion for the film thickness and which leads to a fourth order in space, first order in time parabolic partial differential equation for the film thickness. This equation is also often referred to as the thin film equation and it has been successful in describing dewetting processes quantitatively [5]. Flow over chemical substrate inhomogeneities has been studied in the context of dewetting of unstable films [17] but to little extent for the actual situations relevant to microfluidics and nanofluidics [7, 19].

4 Conceptual differences in microfluidics and nanofluidics

In this section we state three important conceptual differences between microfluidics and nanofluidics.

4.1 Triple line and chemical steps

One of the most critical issues in open microfluidic systems is to keep the liquid in the desired areas such as channels, reactors, and reservoirs. On a macroscopic scale the liquid will stay on the lyophilic channels for low filling and the three phase contact line will lie on the channel area or it will be pinned at the chemical step. Spill-over onto the lyophobic areas occurs once the contact angle of the liquid at the chemical step exceeds the advancing contact angle $\alpha_a$ on the lyophobic area (which is in general larger than the equilibrium contact angle $\alpha_e$ due to surface defects).

On the nano-scale the situation is quite different. First, the concepts of a contact line and contact angle have to be revised. A sharp contact line is replaced by a smooth transition from a mesoscopic wetting film to the precursor film [4] [18] [13] [2] [3] which is only some few molecular diameters thick and spreads ahead of the main portion of the moving liquid. Moreover even an atomically sharp boundary between lyophilic and lyophobic areas on the substrate will lead to a smooth lateral variation of the interaction potential between the liquid particles and the substrate.

Thus the macroscopic and sharp criterion for a liquid staying on a chemical channel, namely whether the triple line crosses the channel boundary or not, becomes fuzzy at the nano-scale. Since there is always a certain amount of liquid on the lyophobic part of the substrate, one has to address
(a) no spillage (b) small tail

10 µm

(c) spillage (d) large tail

100 nm

Figure 2: Spill-over of a liquid channel on a micron-sized chemical strip (left column) as compared to a nano-scale strip (right column). Dark grey marks the lyophobic areas and light grey the lyophilic areas. At the micron scale one can clearly distinguish between no spillage (a) and spillage (c), whereas for nano-channels one can only distinguish between small tails (b) and large tails (d) of the lateral liquid distribution.

the issue which fraction of the liquid is outside the channels rather than whether there is liquid outside the channels.

4.2 Interaction between neighboring channels

The question of spillage is of course closely related to the question of interaction between neighboring channels. Macroscopically (neglecting evaporation and recondensation) two neighboring channels will interact once the two liquid films merge. One has to keep in mind that in a macroscopic description an empty and a filled channel next to each other (Fig. 3(e)) or two filled but not interacting channels (Fig. 3(a)) can be metastable states. In the first case two equally filled channels and in the second case a liquid bridge can be the equilibrium state. How such configurations are affected by flow has not been investigated yet.

On the nano-scale, however, tails of the liquid from two neighboring channels can leak onto the lyophobic area between the channels. If the channels are too close these tails will overlap and thus form a bridge (see Fig. 3(b) and (d)). Liquid can flow through such a bridge and particles immersed in the fluid can diffuse through these bridges. Thus keeping the two flows separated is a question of time-scales and not a question that can be answered definitively.

Also the presence of a monomolecular precursor film on the lyophobic area can lead to an exchange of molecules (see Fig. 3(f)). Macroscopically this is certainly negligible but since the ratio between the film thickness in the channel and the thickness of the precursor film can be of the order
Figure 3: Interaction between neighboring channels at the micron scale (left column) and at the nano-scale (right column). Dark grey marks the lyophobic areas and light grey the lyophilic areas. At the micron scale the flows are either well separated (a) or merged (c). Even a filled channel next to an empty one (e) is possible. At the nano-scale the tails of the liquid in the channels will merge and thus form a thin (b) or thick (d) bridge through which material can be interchanged. The thickness of the bridge is that of a monolayer in the case of a precursor film (f).
of 10, this can be significant at the nano-scale.

Fluctuations also become more important at small scales. In the absence of a precursor film on the area between the channels, a filled channel next to an empty one can be a metastable state as in the macroscopic case discussed above. But the energy barrier which has to be overcome to connect the two channels is much smaller than for macroscopic distances and much smaller fluctuations of the film height are needed.

Not only the liquid-substrate interactions but also the liquid-liquid interaction has a range of up to 100 nm. Thus the direct interaction between liquid streams in parallel channels will influence the flow and also the thermal fluctuations.

4.3 Flow and the atomistic structure of liquids

The conclusions in the last two subsections are mostly based on quasi-static considerations. Transport mechanisms and dynamic properties have not been discussed. Experience tells that down to length scales of about 1–10 nm hydrodynamic theories provide a quite good description of liquid flow. However, even at the micron scale atomistic properties of the liquid show up via the slip length at the liquid-substrate interface and via the details of the regularization of the stress singularity at the moving triple line (see Fig. 4(a)).

In nanofluidic systems there is a window of length scales within which long-ranged intermolecular forces play a role and hydrodynamics is still applicable. This window is centered around film thicknesses of about
100 nm. Below this length scale the atomistic structure of the liquid comes into play. Currently only molecular dynamics simulations explore this atomic length scale region (see for example Fig. 4(b)).

5 Design issues for nanofluidics

For liquid flow inside chemically patterned micron-sized channels several design issues have been addressed [29]. Due to the conceptual differences between flow on the micron scale and flow on the nano-scale the answers given for the micron scale cannot be transferred directly to the nano-scale. However, the basic issues are the same: (1) How much liquid can a chemical channel contain before considerable spillage onto the lyophobic areas occurs? (2) How wide must the channels be to support flow? (3) How small can the radius of curvature of bends in the channel be? (4) What is the minimum distance between liquid streams below which they interact?

In micron scale channels these issues can be addressed by considering only surface tensions, contact angles, and line tensions. On the nano-scale the situation is more complex. In particular the details of the interaction between liquid and substrate, the interaction among the liquid molecules, the influence of the atomistic structure of the fluid on the transport properties, and thermal fluctuations have to be taken into account in addition.

References

[1] C. Bauer and S. Dietrich, Quantitative study of laterally inhomogeneous wetting films, Eur. Phys. J. B 10, 474–480 (1999).
[2] C. Bauer, Benetzung chemisch strukturierter Substrate, Ph.D. thesis, Bergische Universität-Gesamthochschule Wuppertal (1999).
[3] C. Bauer and S. Dietrich, Wetting films on chemically heterogeneous substrates, Phys. Rev. E 60, 6919–6941 (1999).
[4] C. Bauer and S. Dietrich, Phase diagram for morphological transitions of wetting films on chemically structured substrates, Phys. Rev. E 61, 1664–1669 (2000).
[5] J. Becker, G. Grün, R. Seemann, H. Mantz, K. Jacobs, K. R. Mecke and R. Blossey, Complex dewetting scenarios captured by thin-film models, Nature Materials 2, 59–63 (2003).
[6] M. Brinkmann and R. Lipowsky, Wetting morphologies on substrates with striped surface domains, J. Appl. Phys. 92, 4296–4306 (2002).
[7] L. Brusch, H. Kühne, U. Thiele and M. Bär, Dewetting of thin films on heterogeneous substrates: Pinning versus coarsening, Phys. Rev. E 66, 011602 (2002).
[8] A. A. Darhuber, S. M. Troian and W. W. Reisner, Dynamics of capillary spreading along hydrophilic microstripes, Phys. Rev. E 64, 031603 (2001).
[9] S. Dietrich, New physical phases induced by confinement, *J. Phys.: Condens. Matter* **10**, 11469–11471 (1998).

[10] S. Dietrich, Fluids in contact with structured substrates. In: *New approaches to old and new problems in liquid state theory*, eds. C. Cacccamo, J. P. Hansen and G. Stell, Kluwer, Dordrecht 1999, vol. C529 of NATO-ASI Series C, pp. 197–244.

[11] R. Evans, Microscopic theories of simple fluids and their interfaces. In: *Liquids at Interfaces*, eds. J. Charvolin, J. F. Joanny and J. Zinn-Justin, Elsevier, Amsterdam 1990, Les Houches Session XLVIII, pp. 1–98.

[12] H. Gau, S. Herminghaus, P. Lenz and R. Lipowsky, Liquid morphologies on structured surfaces: From microchannels to microchips, *Science* **283**, 46–49 (1999).

[13] T. Getta and S. Dietrich, Line tension between fluid phases and a substrate, *Phys. Rev.* **E 57**, 655–671 (1998).

[14] N. Giordano and J.-T. Cheng, Microfluidic mechanics: progress and opportunities, *J. Phys.: Condens. Matter* **13**, R271–R295 (2001).

[15] K. Handique, D. T. Burke, C. H. Mastrangelo and M. A. Burns, Nanoliter liquid metering in microchannels using hydrophobic patterns, *Anal. Chem.* **72**, 4100–4109 (2000).

[16] N. L. Jeon, D. T. Chiu, C. J. Wargo, H. Wu, I. S. Choi, J. R. Anderson and G. M. Whitesides, Design and fabrication of integrated passive valves and pumps for flexible polymer 3-dimensional microfluidic systems, *Biomedical Microdevices* **4**, 117–121 (2002).

[17] K. Kargupta and A. Sharma, Templating of thin films induced by dewetting on patterned surfaces, *Phys. Rev. Lett.* **86**, 4536–4539 (2001).

[18] W. Koch, S. Dietrich and M. Napiórkowski, Morphology and line tension of liquid films adsorbed on chemically structured substrates, *Phys. Rev.* **E 51**, 3300–3317 (1995).

[19] L. Kondic and J. A. Diez, Flow of thin films on patterned surfaces: Controlling the instability, *Phys. Rev.* **E 65**, 045301 (2002).

[20] J. Koplik, unpublished.

[21] P. Lam, K. J. Wynne and G. E. Wnek, Surface-tension-confined microfluidics, *Langmuir* **18**, 948–951 (2002).

[22] P. Lenz and R. Lipowsky, Stability of droplets and channels on homogeneous and structured surfaces, *Eur. Phys. J. E* **1**, 249–262 (2000).

[23] K. R. Mecke and S. Dietrich, Effective hamiltonian for liquid-vapor interfaces, *Phys. Rev.* **E 59**, 6766–6784 (1999).

[24] P. Mitchell, Microfluidics—downsizing large-scale biology, *Nature Biotech.* **19**, 717–721 (2001).

[25] A. Oron, S. H. Davis and S. G. Bankoff, Long-scale evolution of thin liquid films, *Rev. Mod. Phys.* **69**, 931–980 (1997).

[26] L. M. Pismen, Mesoscopic hydrodynamics of contact line motion, *Colloids Surf. A: Physicochem. Eng. Aspects* **206**, 11-30 (2002).
[27] H. A. Stone and S. Kim, Microfluidics: Basic issues, applications, and challenges, *AIChE J.* 47, 1250–1254 (2001).

[28] A. Valencia, M. Brinkmann and R. Lipowsky, Liquid bridges in chemically structured slit pores, *Langmuir* 17, 3390–3399 (2001).

[29] B. Zhao, J. S. Moore and D. J. Beebe, Principles of surface-directed liquid flow in microfluidic channels, *Anal. Chem.* 74, 4259–4268 (2002).