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PAPER

Suppressing the coffee stain effect: how to control colloidal self-assembly in evaporating drops using electrowetting†

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We study the influence of electrowetting on the formation of undesired solute residues, so-called coffee stains, during the evaporation of a drop containing non-volatile solvents. Electrowetting is found to suppress coffee stains of both colloidal particles of various sizes and DNA solutions at alternating (AC) frequencies ranging from a few Hertz to a few tens of kHz. Two main effects are shown to contribute to the suppression: (i) the time-dependent electrostatic force prevents pinning of the three phase contact line and (ii) internal flow fields generated by AC electrowetting counteract the evaporation driven flux and thereby prevent the accumulation of solutes along the contact line.

Introduction

Evaporating drops of colloidal suspensions and solutions of non-volatile species leave behind ring-like solid residues along the contact line.^{1,2} This coffee stain effect—named after the most widely known representative of this class of structures—leads to an undesired inhomogeneous distribution of solutes, commonly encountered in coating and printing applications involving volatile solvents. Combinatorial analysis methods such as fluorescent microarrays^{3,4} and MALDI-MS⁵ are specific examples where the inhomogeneity of the residual deposits compromises the overall performance of a system. In other applications capillarity-driven assembly of colloidal and macromolecular species upon solvent evaporation can also be desirable to generate surface patterns.^{6–9} In a seminal work, Deegan *et al.*¹ pointed out that the physical origin of the coffee stain effect is due to a combination of pinning of the three-phase contact line and a convective flux driven by the evaporation. In the present communication, we demonstrate that the formation of coffee stains can be suppressed by applying electrowetting (EW) with an alternating (AC) voltage to an evaporating drop. For optimized AC frequencies in the range of a several tens of Hz to a few kHz, the residue of a typical millimetre-sized drop consists of a much

smaller, single, homogeneous spot of the solute rather than the irregular coffee stain.

Experimental section

Electrowetting setup

The experiments are performed on glass substrates with a transparent Indium Tin Oxide (ITO) layer as an electrode. The electrodes are covered with a 5 μm thick layer of SU8, which displays an advancing and receding contact angle of $\theta_a = 85^\circ$ and $\theta_r = 60^\circ$, respectively. In the standard electrowetting configuration the electrode on the substrate is electrically grounded and the voltage is applied to the drop by immersing a 50 μm diameter Pt wire all the way to the bottom of the drop. In the wire-free configuration, the ITO is patterned lithographically into sets of interdigitated electrodes with a pitch of 30 μm . An applied voltage with a fixed root-mean-square amplitude $U_{\text{rms}} = 200 \text{ V}$ is applied throughout at frequencies varying from 6 Hz to 100 kHz. The experiments are carried out at an ambient temperature of $23 \pm 2^\circ\text{C}$ under a transparent plastic box (diameter approx. 5 cm) to block air currents. The evaporating drop is monitored from two different directions: bottom and side view. The contact angle measurements were from the side view and the radius, velocity measurements were from the bottom view. The fast movements of the 5 μm particles inside the droplet were recorded using a high speed camera (Photron fastcam SA3). By using particle tracking techniques,²⁴ the trajectories of the particles were analyzed to obtain the average flow speeds inside the drop given in Fig. 4.

Materials

Aqueous solutions were prepared using deionised (Millipore) water. 10 mM of LiCl was added to adjust the conductivity of the solution to 2 mS cm^{-1} . Colloidal suspensions of fluorescently labelled carboxyl terminated polystyrene particles (Polysciences

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§ MALDI-MS stands for Matrix Assisted Laser Desorption Ionization Mass Spectroscopy.

Inc.) ranging from 0.1 μm to 5 μm in diameter are prepared with a volume fraction of 0.05%. DNA solutions with a concentration of 2.5 $\text{ng } \mu\text{L}^{-1}$ are prepared by diluting a fluorescently labelled (SYTO 24) stock solution of cDNA with deionised water in a 4 : 1 ratio. Experiments with colloidal particles made of PMMA and silica also produced quantitatively same results.

Results

To understand the success of EW in suppressing coffee stains, we first recapitulate the various evaporation scenarios of sessile drops. For perfectly flat surfaces without any contact angle hysteresis drops evaporate at a constant contact angle: as solvent evaporates, the surface of the drop (including the three phase contact line) simply recedes according to the amount of mass lost to the vapour phase. In this case non-volatile solutes collect in a single spot, *i.e.* without leaving behind a coffee stain. In the more frequent situation of finite contact angle hysteresis, however, the contact line is pinned at defects and cannot recede as the solvent is lost due to evaporation. Mass conservation therefore requires that the additional solvent is transported from the center of the drop towards the contact line. This flux transports more solute towards the contact line. The resulting local increase in the solute concentration can lead to an enhanced viscosity and/or to precipitation of the solute. The precipitated solute further enhances the pinning forces and it ultimately forms the solid residue that constitutes the coffee stain (see Fig. 1). Depending on the initial contact angle hysteresis and the rate at which the pinning forces increase, the contact line either remains stuck during the entire evaporation process or displays a stick-slip motion involving one or more pinning-depinning cycles.^{10,11}

The drops considered here, aqueous colloidal suspensions (0.05 vol%) of fluorescently labelled polystyrene or other particles of various sizes or solutions of DNA (see Experimental section for details) on SU8 substrates, leave behind round coffee stains if left alone to evaporate without EW. A few typical examples are shown in the first column of Fig. 2. Due to the moderate hydrophobicity of SU8, the drop belongs to the class of intermediate systems. The black squares in Fig. 3 illustrate the three phases of evaporation for a drop evaporating on SU8: (i) for $0 < \tau < 0.2$ radius of the droplet (R) is essentially constant and the contact angle (θ) decreases where τ is the time normalized by the total evaporation time t_{evap} , which is approximately 10 min. (ii) For $0.2 < \tau < 0.8$ R decreases and θ is constant. (iii) In the final stage, for $0.8 < \tau$ R displays another plateau value and θ decreases to zero. The coffee stain is formed in the final stage for $0.8 < \tau < 1$. The typical velocities of the evaporation-driven flow^{1,2} are of the order 10–20 $\mu\text{m s}^{-1}$ during most of the evaporation process with a typical steep increase for $\tau \rightarrow 1$ (see black squares in Fig. 4).

According to the above discussion, coffee stains are formed due to the combination of contact line pinning and the resulting flux of solvent and solute towards the contact line. Previous strategies to overcome the coffee stain effect focused either on the elimination of contact line pinning by using low hysteresis materials^{4,5} and by mechanical shaking or on the generation of internal flow patterns to counteract the evaporation driven flux with surface tension gradient driven “Marangoni flows”¹² and with electroosmotic flows.¹³ Electrowetting can be particularly efficient at counteracting coffee stain formation because it offers the unique possibility of addressing both aspects simultaneously. Electrowetting can indeed set pinned contact lines in motion and

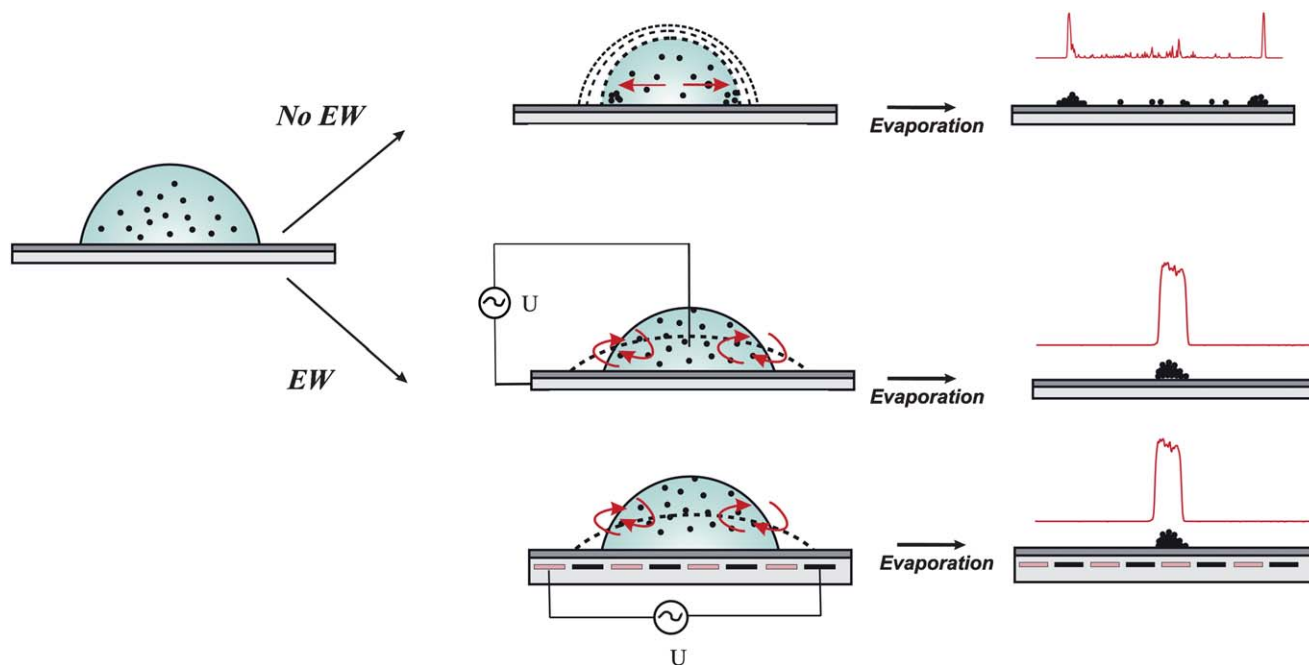


Fig. 1 Schematic of the drop evaporation process. Top row represents evaporation without electrowetting and with contact line pinning; middle and bottom panels show the process with electrowetting and mobile contact lines. The middle panel illustrates the conventional EW setup whereas the bottom panel illustrates the alternative wire-free geometry of EW using interdigitated electrodes. Right column: schematic and experimental intensity cross-sections (solid lines) through the residue. Experimental data taken from Fig. 2a and c.

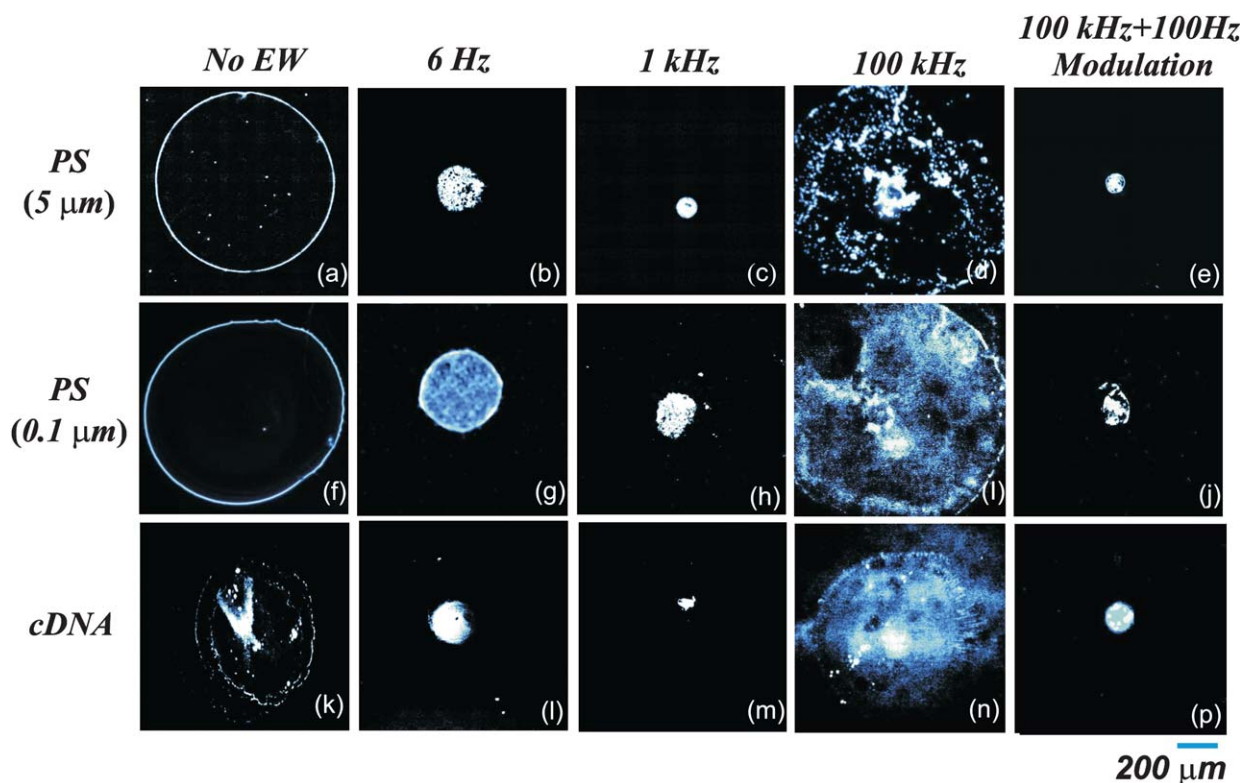


Fig. 2 Suppression of the coffee stain effect illustrated for different materials at three frequency regimes (6 Hz, 1 kHz, 100 kHz) and an amplitude modulation (100 kHz with 100 Hz modulation). Panels a–p show the residual patterns for various materials under different frequency regimes. Panels a–e, Panels f–j and Panels k–p demonstrate the suppression of coffee stain for 5 μm and 0.1 μm diameter polystyrene particles and fluorescently labelled cDNA respectively.

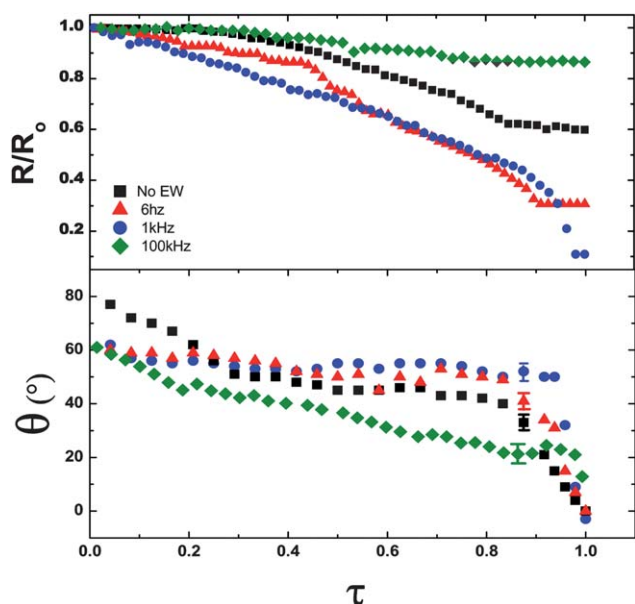


Fig. 3 Normalized radius (R/R_0) of evaporating drop (top panel) and contact angle (θ) (bottom panel) as a function of normalized time (τ) for different frequency regimes described in the main text. Time is normalized with respect to the time required for complete evaporation and radius is normalized with respect to the initial drop radius (R_0). The solute used in this experiment is 5 μm diameter carboxylate terminated polystyrene particles dispersed in Millipore water with 10 mM LiCl.

eliminate the contact angle hysteresis.¹⁴ In addition, EW can generate internal flow fields within sessile drops.^{15–18}

Electrowetting¹⁹ is known to be a particularly versatile tool to manipulate drops of conductive liquids such as water as well as a variety of other highly polarizable solvents.²⁰ EW provides a unique way to exert forces directly to the contact line of sessile drops. For the generic electrowetting geometry of a drop

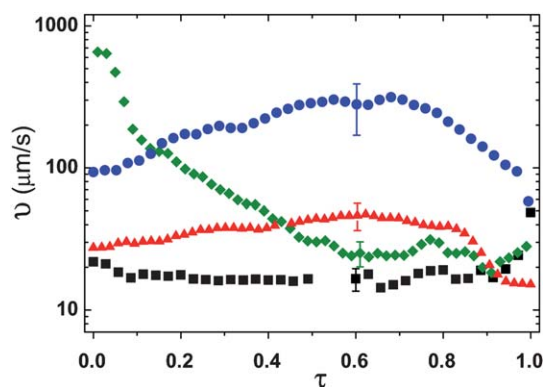


Fig. 4 Average particle velocity (v) as a function of normalized time (τ) for different frequency regimes and the reference experiment where no EW is applied. The single error bars indicate the distribution of particle velocity throughout the evaporation process. The solute used in experiment is 5 μm diameter carboxylate terminated polystyrene particles dispersed in Millipore water with 10 mM LiCl.

deposited on a dielectric layer of thickness d and dielectric constant ϵ_d covering an electrode, applying a voltage U between the drop and the electrode gives rise to an electric force per unit length pulling outward on the contact line that can be written as $f_{el} = \epsilon_d \epsilon_0 U^2 / 2d$ (ϵ_0 : vacuum permittivity). In fact, this force is distributed over a range of order d around the contact line. Yet, for a typical drop radius $R \gg d$, this effect can be neglected if we consider only the global response of the drop.²¹ Inserting f_{el} into the force balance at the three-phase contact line gives rise to the well-known electrowetting equation, which describes the reduction of the contact angle θ as a function of the applied voltage:

$$\cos \theta = \cos \theta_Y + \eta \quad (1)$$

Here, $\eta = f_{el}/\sigma$ is the dimensionless electrowetting number, σ is the surface tension of the drop and θ_Y is the Young's angle. In the presence of contact angle hysteresis, eqn (1) has to be complemented by a pinning force of a random magnitude $\pm f_p$ that counteracts any contact line motion. The strength of the pinning force is related to the macroscopic contact angle hysteresis by $f_p = \sigma(\cos \theta_a - \cos \theta_r)$, where θ_a and θ_r are the advancing and the receding contact angle. For the present samples, we have $f_p \approx 0.35\sigma$. Pinned contact lines can be set in motion by applying an electric force that exceeds the maximum pinning force, *i.e.* by applying a sufficiently high voltage. In EW devices pinning forces typically lead to a finite threshold voltage to initiate drop motion (see Mugele and Baret¹⁹ and references there).

As we ramp up and down the applied voltage at frequencies far below the lowest eigenfrequency of the drop, the contact angle and drop radius follow the driving force quasistatically. Using a maximum voltage of $U = 200$ V ($\eta = 0.8 > 0.35$), the contact line keeps moving and the contact radius keeps decreasing up to times $\tau > 0.95$ (see red triangles in Fig. 3). As the drop evaporates the concentration of solute along the contact line keeps increasing (see Movie S1 in the ESI†). When the electric force f_{el} can no longer move the contact line, the contact line remains pinned at $R/R_0 \approx 0.3$. The residue is thus more homogeneously concentrated in a single spot and the second column of Fig. 2 shows that the fluorescence intensity is much more homogeneously distributed than without EW.

To improve the situation further, it is necessary to prevent the accumulation of the solute at the contact line. This can only be achieved by overcoming the evaporation-driven flow field within the drops. EW can generate flow fields in two different ways: *via* excitation of eigenmodes or by electrothermal effect. For driving frequencies in the range of several tens of Hz to a few kHz,^{15,17} the excitation of eigenmodes^{16,22} and/or propagating capillary waves¹⁵ at the drop surface can drive internal flows with maximum flow velocities of several hundred $\mu\text{m s}^{-1}$ (blue circles in Fig. 4). These flows are driven by a purely hydrodynamic mechanism, in which the drop is forced by the time-dependent electric force f_{el} acting on the contact line. As a result, fewer particles accumulate along the contact line and the solid residue is concentrated in an even smaller spot ($R/R_0 = 0.1$) than for the quasi-static actuation, as shown by the blue circles in the top panel in Fig. 3a as well as column 3 of Fig. 2. The blue circles in Fig. 4 show that the hydrodynamic flows are approximately one order of magnitude stronger as compared to the zero voltage and quasi-static EW throughout almost the entire evaporation process. This strong

flow completely prevents any solidification/jamming due to increasing solute concentration²³ along the contact line. The shear forces generated by the flow are even strong enough to erode/unjam preformed precipitates at the contact line, as can be seen if EW is activated only at $\tau = 0.5$ (see Movie S2 of ESI†).

EW can also generate hydrodynamic flow fields *via* electrothermal effect at AC frequencies of order 100 kHz and above for poorly conductive liquids. However, the physical mechanism driving these high frequency flows (100 kHz) is completely different: at these high frequencies and low conductivities, electric fields penetrate into the liquid leading to Ohmic currents and local heating of several degrees within the drop. The resulting temperature gradients along with the electric fields give rise to electrothermal flows.^{17,18} The electrothermal excitation does lead to somewhat less pronounced coffee stains than the undisturbed evaporation case but does not succeed in reducing the spot size (see column 4 in Fig. 2). We attribute the poor performance of the high frequency excitation to a combination of two effects. First of all, Fig. 4 shows that the initially high flow speed rapidly decays as the evaporation proceeds. This decrease is probably due to the inevitable increase of the conductivity of the liquid as the salt concentration increases upon solvent evaporation. It results in better screening of the electric field and hence the electrothermal driving force decreases. Second, at the very high driving frequencies inertia prevents any net motion of the drop. Hence the contact line can be pinned more easily. The latter problem can be eliminated by modulating the amplitude of the high frequency excitation with a low frequency. The fifth column of Fig. 2 shows that a 100 Hz amplitude modulation of a 100 kHz carrier excitation indeed produces very small and concentrated drop residues. Since the high frequency excitation also speeds up the evaporation process (by approximately a factor 2 in the present experiments) this combination may be desirable in applications that are not harmed by temperature increases up to 10 or 20 °C.

Discussion

All results do not depend very sensitively on the exact value of the AC frequency. The behaviour reported refers to three different frequency regimes: (i) the quasistatic regime at frequencies below the lowest eigenfrequency of the drop, *i.e.* typically up to about 10 Hz for millimetre-sized drops; (ii) the hydrodynamic regime in the range of the eigenfrequencies of the drop from several tens of Hz to a few kHz; (iii) the electrothermal regime at frequencies allowing for penetration of the electric field into the bulk of the liquid. Achieving the smallest residue spots requires a combination of moving contact lines to prevent pinning and of internal flow fields to avoid solute accumulation along the contact line. This is best achieved in the hydrodynamic regime or by a combination of high frequencies with low frequency amplitude modulation.

In applications such as microarrays the presence of the wire which is immersed into the drop in the standard configuration of EW is frequently inconvenient. Yet, this wire can be eliminated by using interdigitated electrodes embedded into the substrate instead (see Movie S3 of ESI†). Test experiments demonstrate that the coffee stain effect can be perfectly suppressed for arrays

of drops evaporating in such a wire-free configuration for driving frequencies in the hydrodynamic regime (see ESI†).

Compared to other approaches of suppressing the coffee stain effect,^{4,5,11,12} EW has the disadvantage that it requires conductive (or highly polarizable) liquids. Yet, the experiments reported here demonstrate that the mechanism works very efficiently for even deionised water, which is the most important solvent for biological applications. EW has the practical advantage that it is non-invasive *i.e.* it neither requires specific additives to the system such as surfactants nor does it require or generate heating if operated in the most successful hydrodynamic frequency range. Furthermore, the liquid is not in direct contact with electrodes which is a desirable feature while working with biological systems. (At first sight the applied voltages may seem high, yet it is important to note that there are not net currents flowing in the system and that most of the voltage drops across the insulating layer. Only a small fraction drops within (the Debye layer of) the liquid and many Lab-on-a-Chip applications of EW¹⁹ demonstrate that this is not a concern for handling biological samples.)

The extension to other substrate materials is currently being explored. Earlier successes regarding the reduction of contact angle hysteresis for a variety of polymer materials are promising.^{14,25} The possibility of applying arbitrary waveforms for the excitation of the drops such as the high frequency with amplitude modulation demonstrates the flexibility of EW (see Movie S4 in the ESI†). This suggests that even more flexible control of the solute assembly in evaporating drops can be achieved in the future, *e.g.* by combining specific waveforms with custom-shaped electrode geometries.

Conclusions

Our results demonstrate that electrowetting is a very efficient tool for suppressing the coffee stain effect in evaporating drops of complex fluids. AC frequencies in the kHz range that promote strong internal flows while preserving the perfect conductor character of the liquid turn out to be the most efficient. Interdigitated electrodes allow for an easy wire-free implementation

of the approach as required for the purpose of many high throughput combinatorial analysis systems.

References

- 1 R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, *Nature*, 1997, **389**, 827–829.
- 2 E. Adachi, A. S. Dimitrov and K. Nagayama, *Langmuir*, 1995, **11**, 1057–1060.
- 3 G. McHale, *Analyst*, 2007, **132**, 192–195.
- 4 R. Blossey and A. Bosio, *Langmuir*, 2002, **18**, 2952–2954.
- 5 Y. Kim, G. B. Hurst, M. J. Doktycz and M. V. Buchanan, *Anal. Chem.*, 2001, **73**, 2617–2624.
- 6 S. Choi, S. Stassi, A. P. Pisano and T. I. Zohdi, *Langmuir*, 2010, **26**, 11690–11698.
- 7 M. Layani, M. Gruchko, O. Milo, I. Balberg, D. Azulay and S. Magdassi, *ACS Nano*, 2009, **3**, 3537–3542.
- 8 H. Bodiguel, F. Doumenc and B. Guerrier, *Langmuir*, 2010, **26**, 10758–10763.
- 9 J. X. Huang, A. R. Tao, S. Connor, R. R. He and P. D. Yang, *Nano Lett.*, 2006, **6**, 524–529.
- 10 I. I. Smalyukh, O. V. Zribi, J. C. Butler, O. D. Lavrentovich and G. C. L. Wong, *Phys. Rev. Lett.*, 2006, **96**, 177801.
- 11 L. Shmuylovich, A. Q. Shen and H. A. Stone, *Langmuir*, 2002, **18**, 3441–3445.
- 12 H. Hu and R. G. Larson, *J. Phys. Chem. B*, 2006, **110**, 7090–7094.
- 13 S. J. Kim, K. H. Kang, J. G. Lee, I. S. Kang and B. J. Yoon, *Anal. Chem.*, 2006, **78**, 5192–5197.
- 14 F. Li and F. Mugele, *Appl. Phys. Lett.*, 2008, **92**, 244108.
- 15 F. Mugele, J. C. Baret and D. Steinhäuser, *Appl. Phys. Lett.*, 2006, **88**, 204106.
- 16 S. H. Ko, S. J. Lee and K. H. Kang, *Appl. Phys. Lett.*, 2009, **94**, 194102–194103.
- 17 S. H. Ko, H. Lee and K. H. Kang, *Langmuir*, 2008, **24**, 1094–1101.
- 18 P. Garcia-Sanchez, A. Ramos and F. Mugele, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2010, **81**.
- 19 F. Mugele and J. C. Baret, *J. Phys.: Condens. Matter*, 2005, **17**, R705–R774.
- 20 D. Chatterjee, B. Hetayothin, A. R. Wheeler, D. J. King and R. L. Garrell, *Lab Chip*, 2006, **6**, 199–206.
- 21 F. Mugele and J. Buehrle, *J. Phys.: Condens. Matter*, 2007, **19**, 375112.
- 22 J. M. Oh, S. H. Ko and K. H. Kang, *Langmuir*, 2008, **24**, 8379–8386.
- 23 H. B. Eral, D. van den Ende, F. Mugele and M. H. G. Duits, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2009, **80**, 061403.
- 24 I. F. Sbalzarini and P. Koumoutsakos, *J. Struct. Biol.*, 2005, **151**, 182–195.
- 25 D. J. C. M. t. Mannetje, C. U. Murade, D. van den Ende and F. Mugele, *Appl. Phys. Lett.*, 2011, **98**, 014102–014103.