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Electrowetting of liquid marbles

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Abstract

Electrowetting of water drops on structured superhydrophobic surfaces are known to cause an irreversible change from a slippy (Cassie-Baxter) to sticky (Wenzel) regime. An alternative approach to using a water drop on a super-hydrophobic surface to obtain a non-wetting system is to use a liquid marble on a smooth solid substrate. A liquid marble is a droplet coated in hydrophobic grains, which therefore carries its own solid surface structure as a conformal coating. Such droplets can be considered as perfect non-wetting systems having contact angles to smooth solid substrates of close to 180^{o}. In this work we report the electrowetting of liquid marbles made of water coated with hydrophobic Lycopodium grains and show that the electrowetting is completely reversible. Marbles are shown to return to their initial contact angle for both ac and dc electrowetting and without requiring a threshold voltage to be exceeded. Furthermore, we provide a proof-of-principle demonstration that controlled motion of marbles on a finger electrode structure is possible.

PACS: 68.08

Keywords: electrowetting, liquid marbles, superhydrophobic

1. Introduction

A small droplet of a liquid deposited on a surface either forms a spherical cap shape with a well-defined equilibrium contact angle θ_e to the solid or it spreads across the surface until it forms a wetting film. The equilibrium that results is determined by a balance between the interfacial forces for the liquid-vapour (γ_{LV}), solid-vapour (γ_{SV}) and solid-liquid (γ_{SL}) interfaces. This equilibrium can be ascribed to the balancing of the relative interfacial contact areas given the interfacial tensions for a particular solid-liquid-vapour system, so as to minimise the surface free energy [1-3]. If a solid surface is physically structured through either patterning or roughness such that the ratio of actual surface area to the geometric (horizontally projected) surface area r is greater than 1, then the effect is to enhance the wetting properties of the flat surface [4]. Wenzel's equation, $\cos\theta_r = r \cos \theta_e$ gives the equilibrium contact angle on the rough surface θ_r as a function of the contact angle on a flat surface θ_e and the surface roughness r, provided intimate contact is maintained between the solid and the liquid. Wenzel's equation predicts that the basic wetting behaviour of a surface will be enhanced by roughness so that roughness on a surface with $\theta_e>90^o$ will result in a larger angle and roughness on a surface with $\theta_e<90^o$ will result in a smaller angle. In practice, intimate contact is not usually maintained on high roughness hydrophobic surfaces, unless hydrostatic pressure is applied. For these surfaces the liquid drop effectively sits upon a composite surface of the peaks of the topography and the air separating the surface features so that the Cassie-Baxter equation applies $\cos\theta_r= f \cos \theta_e - (1-f)$ where f is the solid fraction of the area supporting the droplet. Surfaces that combine water repellent surface chemistry with surface structure or roughness can produce super hydrophobic surfaces exhibiting contact angle in excess of 150^o.

In contrast to the increased contact angle obtained through increased surface roughness, a reduced contact angle on a smooth solid surface can be achieved controllably by electrowetting under the application of an applied ac or dc bias voltage. In electrowetting-on-dielectric (EWOD), the solid surface upon which the liquid drop rests is a thin electrical insulator layer of thickness d coating an underlying conducting surface [5]. Thus, a slightly conductive droplet creates a capacitance defined by the contact area of the droplet and the substrate. When a voltage, V, is applied between the substrate and droplet an electric charge is created and this alters the surface free energy balance. The additional energy per unit area due to the capacitance is given by $\frac{1}{2}CV^2$ where for a simple planar surface the capacitance per unit area is $C=\varepsilon_r\varepsilon_o/d$. It is found that for a droplet on a flat surface the equilibrium contact angle for a given voltage is given by the expression $\cos\theta_e(V) = \cos\theta_e+CV^2/(2\gamma_{LV})$; a review of electrowetting has recently been published in [6]. These considerations would suggest at first sight that combining a super-hydrophobic structured surface with electrowetting should give a technique to control the contact angle through a wide angular range. In practice it has been shown that a drop in the Cassie-Baxter form on a patterned surface is converted to the Wenzel regime under the application of a bias voltage and that the Cassie Baxter regime is not re-established on the removal of the applied bias; significant hysteresis has been observed. In addition, a significant threshold voltage must be exceeded in order to initiate the contact angle change [7].

In this work, we suggest that an alternative to placing a drop on a structured surface is to incorporate the structure around the liquid in a conformal coating, so that deformations of the liquid marbles surface caused by an applied voltage become fully reversible on removal of the voltage. Such liquid marbles have been of interest in recent years [8-10]. Liquid marbles are produced when a small quantity of liquid is rolled around in a hydrophobic powder, which causes the powder to spontaneously coat the drop. Liquid marbles are highly mobile and electrostatic and magnetic actuation has been reported, but their use in electrowetting has not been studied. For drops of radius less than the capillary length $\kappa^{-1} = \surd(\gamma_{LV}/\rho g)$, gravity becomes negligible and the marble is a spherical shape. For marbles much greater in size than the capillary length a puddle forms with a limiting height $h = 2\kappa^{-1}$. In this article we report electrowetting of liquid marbles and demonstrate that, unlike wetting on patterned surfaces, contact angle changes may be achieved using both ac and dc bias, without requiring a threshold voltage to be exceeded and without significant hysteresis. We also provide a simple proof-of-principle experiment to demonstrate that controllable motion may be achievable using electrodes embedded entirely within a substrate.

2. Experimental

Lycopodium grains of size d_L=(17±3) μm were hydrophobized by immersing in cyclohexane with added hexamethyldisilizane for 48 hours and then drying in an oven. To create the liquid marbles, superhydrophobic MTEOS foam was cast in the shape of a watch glass [11]. The Lycopodium powder was then dispersed thinly, but evenly over the surface of the watch glass and droplets of deionised water with 0.01M KCl were deposited from a syringe onto the powder. As the droplets were made to roll around they became coated and transformed into highly mobile liquid marbles. These appeared to have a coating consisting of individual grains with water clearly visible between them. These grains provide the conformal coating and ensure the water within the marble does not come into direct contact with any substrate upon which the marble rests. Conceptually, it is as if the topography providing super-hydrophobicity has been transferred from the solid substrate to the liquid surface with the advantage that the topography now deforms itself under the action of surface tension. For the electrowetting experiments the marbles were transferred to a glass substrate that contained a sputter coated Ti/Au electrode with a spin coated polymer overlayer of Shipley S1813 photoresist (thickness 1.5μm and baked at 100 C for 30 minutes) and finally a thin hydrophobic capping layer of Flutec LE15 (thickness ~ 1 μm). The photoresist and Flutec layers provide an insulating layer across the electrodes to guard against the danger that at high electrowetting voltages the water may intrude between the grains, breach the skin of the marble and eventually come into direct contact with the metal surface. For the electrowetting experiments, a thin metal contact wire was brought into contact with the water within the marble from above and a bias voltage applied. Figure 1 shows a schematic of the experimental configuration and also illustrates the separation of the droplet from the substrate provided by the hydrophobic granular coating of the liquid marble. For DC voltages a Keithley 2410 source/meter was used and for ac voltages the output of an Agilent 33220A waveform generator was fed through a Trek PZD700 amplifier. The profile of the drop was captured in silhouette illumination using the drop shape analysis software on a Krüss DSA-1 contact angle meter. Due to the very high contact angle and the texturing of the drop surface caused by the hydrophobic grains, accurate measurement of contact angles proved challenging and required analysis of the images frame by frame rather than using automated fitting routines.

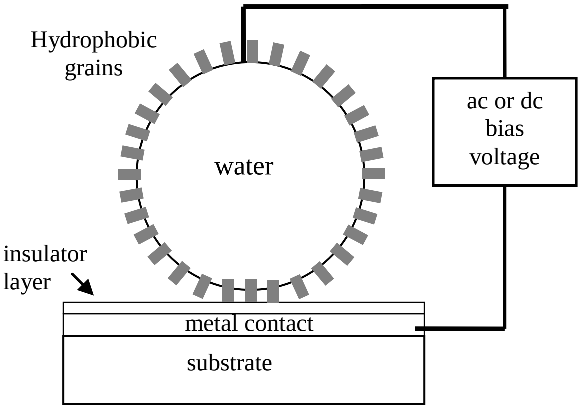

Figure 1. Electrowetting arrangement for a liquid marble. The liquid marble is shown schematically as a perfect spherical droplet with hydrophobic grains providing a separation between the liquid of the marble and the substrate.

In a separate sequence of experiments focussing on actuating droplet motion, we used a glass slide with multiple Ti/Au finger electrodes of width 0.3 mm and spacing 0.3 mm. To obtain motion without requiring a contacting electrode inserted into the marble a dc bias of 150 volts was applied across two series resistors of 10 MΩ. The centre of the resistors was connected to a plate held above the patterned electrode slide; marbles were placed between these two plates resting on the finger electrodes (figure 2a). The +75V and -75V relative to the upper plate were applied sequentially to adjacent electrodes under a 1 μl marble, having a 0.62 mm diameter, with a 10 second delay between changes in applied voltage and a sequence of images was captured showing the motion produced. In these experiments, the finger electrodes were not capped with an insulating coating between the marble and the gold electrodes. Figure 2b shows a full schematic of the equipment together with an inset photograph showing a view from above of the electrode structure. For this photograph the top plate has been moved aside so that a liquid marble can be seen on the electrodes; the direction for actuated motion is across the electrodes.

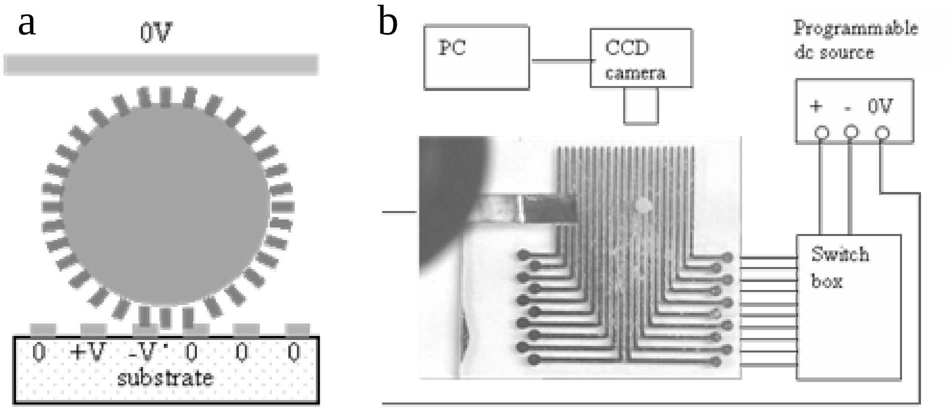

Figure 2. Experimental arrangement for droplet actuation: (a) principle of successive application of voltage (+V, -V) across pairs of fingers with an upper grounded electrode (0V); (b) schematic showing arrangement of equipment together with a top-view photograph of the substrate with electrodes and with a liquid marble (the upper electrode has been moved aside to allow the marble to be seen in the photograph).

3. Results and Discussion

In order to confirm that our system for deposition of marbles was consistent with previous work we produced marbles of radius 0.4 mm through to puddles of radius 5.8 mm. Figure 3 shows the height versus radius for these just after deposition and from this data the limiting height $h = 2\kappa^{-1}$ may be used to estimate the capillary length and, hence, the effective surface tension γ_{LV}. The saturation of height with droplet size yields a capillary length of 2.3 mm compared to 2.7 mm for water, thus requiring a reduction in the effective surface tension due to the hydrophobic lycopodium coating from 72.8 mN/m to 53 mN/m; this data is consistent with the data of Aussillous and Quere [8, 10]. Figure 3 allows a selection of droplet volume to be made so that a good spherical shaped droplet with high apparent contact angle can be obtained; the inset images in figure 3 show a marble of radius 0.68 mm and a puddle of radius 5.71 mm. We emphasise that in both cases the droplet/puddle are completely non-wetting with the water within the marble/puddle separated from the substrate by the hydrophobic powder; the apparent contact angle of less than 180^{o} for the puddle is a consequence of the gravitational flattening of the droplet.

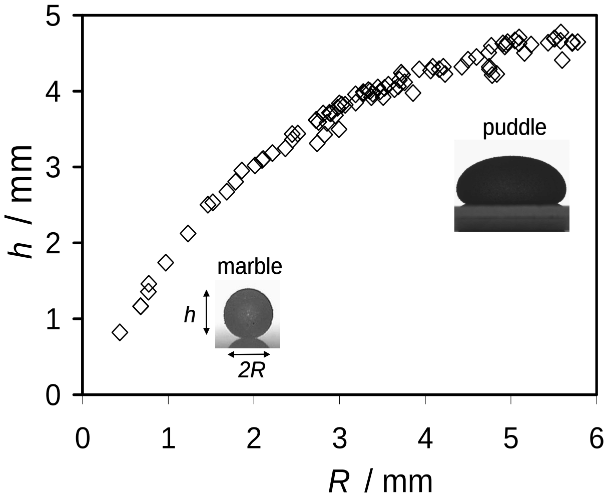

Figure 3 Height as a function of radius for freshly deposited drops converted into marbles; the transition from marble to puddle with increasing volume is shown. Inset are images taken for marble of radius 0.68 mm and puddle of radius 5.71 mm. The limiting value of puddle height gives twice the capillary length.

When electrowetting of marbles was performed, contact area increased. Figure 4a shows an image of a low contact area and high contact angle (θ~174°) liquid marble at zero applied bias and figure 4b shows an image of the same marble with an increased contact area and a reduced contact angle (θ ~147°) due to the application of a 100 V dc applied bias. The fact that the initial contact angle at zero applied bias is less than 180° is entirely a consequence of gravitational flattening. At the highest voltages we applied, liquid appeared to penetrate through grains and some of the Lycopodium grains were ejected from the surface of the liquid marble; if the voltage was increased too high the marble burst. However, by restricting the range of the applied voltage, a marble could be taken through an electrowetting cycle and a reversible change in contact angle achieved. In figure 5a we show the contact angle as a function of dc voltage for a marble of radius 0.78 mm taken through a voltage cycle from zero to 100 V in steps of 20 Volts and with 10 seconds between voltage steps (diamond and square symbols). In electrowetting, AC voltages are often used in preference to DC voltages to minimise hysteresis effects arising from charging. We have therefore also shown in figure 5a the contact angle as a function of rms ac voltage for a marble of radius 0.82 mm taken through a voltage cycle from zero to 200 V peak to peak in steps of 40 volts and with 10 seconds between voltage steps (triangle and circle symbols); this data is consistent with the dc voltage. These results demonstrate that there is no threshold required before electrowetting begins and that it returns to the original contact angle within experimental error. The lack of any threshold voltage before a droplet deforms and the lack of significant hysteresis compared to electrowetting with a liquid droplet is due to the surface structure provided by the hydrophobic lycopodium conforming to the liquid surface rather than the substrate. As the voltage is increased and the marble spreads, more hydrophobic lycopodium grains come into contact with the substrate, but the water within the marble does not. When the voltage is removed, there is effectively no energy barrier to a solid hydrophobic grain detaching from the solid substrate, but the energy needed for a hydrophobic grain to be removed from the liquid-air interface is high [10], thus ensuring the lycopodium conforms to the surface of the marble rather than the surface of the substrate.

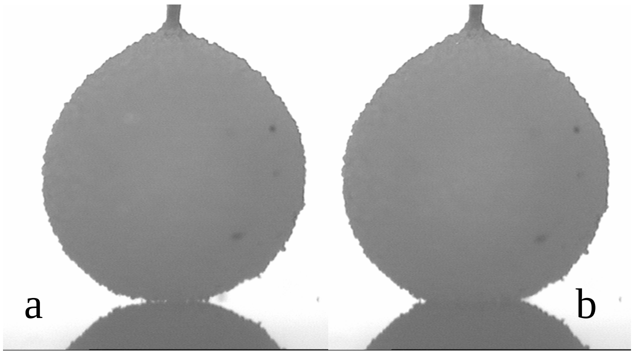

Figure 4. (a) Image of liquid marble with contact wire inserted, but no applied bias voltage; (b) image of the same marble with 100 V dc applied bias.

In Figure 5b we show the data of figure 5a plotted as cosine of the contact angle versus the square of the voltage; the linear relationship confirm that an electrowetting-type relationship holds for the marbles. For electrowetting-on-dielectric of liquid droplets, the slope in figure 5b gives $C/(2\gamma_{LV})$ where $C=\varepsilon_r\varepsilon_o/d$ is the capacitance per unit area, $\varepsilon_r\varepsilon_o$ is the permittivity and d is the thickness of insulator. For a spherical hydrophobic grain of diameter d_L, the length of grain protruding from the liquid-air interface is $d=d_L(1-\cos\theta_L)/2$, where θ_L is the contact angle for the hydrophobic coating on the lycopodium grains. To obtain an order of magnitude estimate for the capacitive effect, we use the slopes of $2.02\text{x}10^{-5}$ V^{-2} and $1.48\text{x}10^{-5}$ V^{-2} and d_L=17 μm with θ_L=110° to give an insulator thickness between the water and the substrate due to the hydrophobic lycopodium grains, to calculate effective values of ε_r=2.8 and ε_r=2.0 for the two sets of data. This calculation can only be considered as an order of magnitude estimate for three reasons. Firstly, the hydrophobic lycopodium powder does not create a uniform insulating layer, but rather a non-densely packed set of grains at the water-air interface. Secondly, the capacitive effects of the photoresist and flutec coatings have been ignored; the estimate could be improved by modelling the system as three series coupled capacitances. Thirdly, the need to take into account gravitational flattening introduces an extra term, dependent on contact angle, into the right hand side of the usual EWOD relationship of $\cos\theta_e(V) = \cos\theta_e + CV^2/(2\gamma_{LV})$ thus creating a non-linear relationship; a theoretical model for this latter effect is given in reference [12]. Nevertheless, the linearity of the plots in figure 5b and the reasonable values from these order of magnitude estimates confirms that the electrowetting of liquid marbles has many similarities to the electrowetting of droplets.

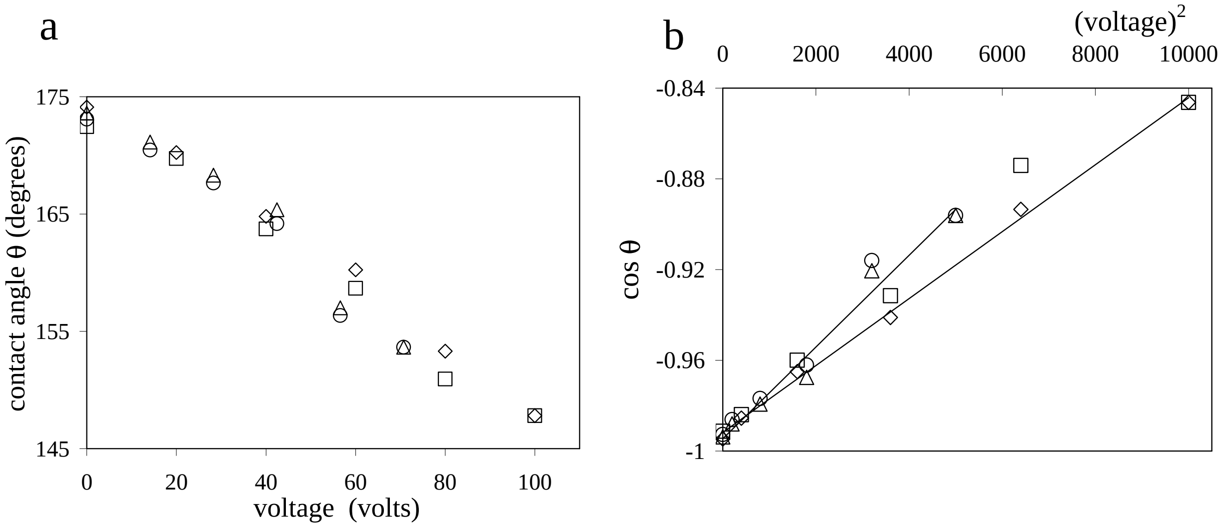

Figure 5. (a) Contact angle as a function of voltage for increasing dc voltage (diamonds), reducing dc voltage (squares), increasing ac (rms) voltage (triangle) and reducing ac (rms) voltage (circles); (b) data shown in figure 5(a) plotted as cosine of the contact angle as a function of the square of the applied voltage.

Figure 6 shows the marble moves on the finger electrode structure as the voltage is applied sequentially to the finger electrodes. Visually, we observed distinctive rolling motion of the marble with it following the actuation of successive pairs of fingers as indicated in figure 2. These results provide a clear proof-of-concept demonstrating that a controlled (digital) actuation may be achieved using this technique, which does not require a direct electrical contact placed into the marble. The images of the marble indicate that charging of some grains is occurring and that some are being ejected from the surface of the marble onto the electrode structure, but we expect improved design of the system could reduce these effects. In this work, we did not systematically investigate the relationship between droplet size and the threshold voltage required to move the marble, nor did we attempt to quantify the maximum speed of displacement that could be obtained, although we are currently performing experiments to determine both of these quantities. The size relationship is of particular interest because Mahadevan and Pomeau discovered that, unlike droplets, liquid marbles become more mobile as their size decreases with velocity scaling inversely to marble radius on a slope with a given incline [10, 13]. The ability to create encapsulated and completely non-wetting droplets with high mobility may provide an alterative to current approaches to droplet microfluidics for small scale chemical and biochemical assays. To do so, further development would be needed to create systems capable of dispensing and extracting of liquids, controlling coalescence and division of marbles and to ensure encapsulated liquids can be adequately mixed.

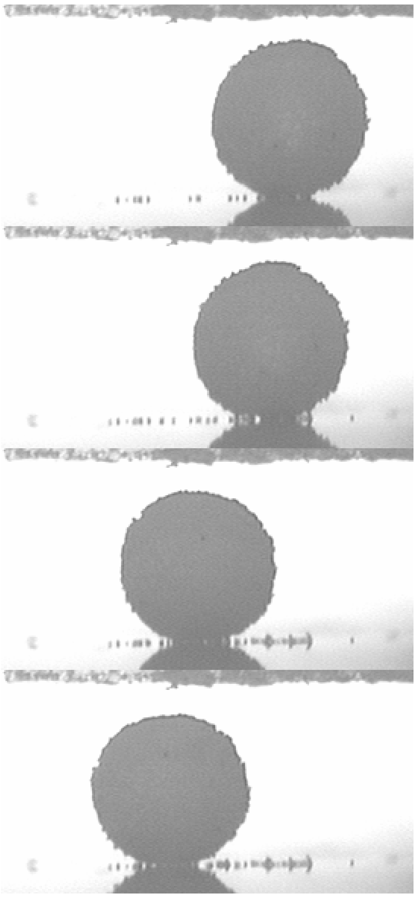

Figure 6. Sequence of images showing a marble rolling due to the application of dc bias to a finger electrode structure under the marble.

4. Conclusion

In this work we have viewed liquid marbles as water drops with conformal coatings, which provide extreme non-wetting in a similar manner to that obtained by the topography of a super-hydrophobic surface. We have demonstrated that for such marbles both ac and dc electrowetting may be achieved. A complete return to the starting contact angle is observed when applied voltage is removed, although some hysteresis is observed between the increasing and reducing voltages. Finally, actuation of liquid marbles has also been demonstrated on a patterned electrode structure.

Acknowledgements

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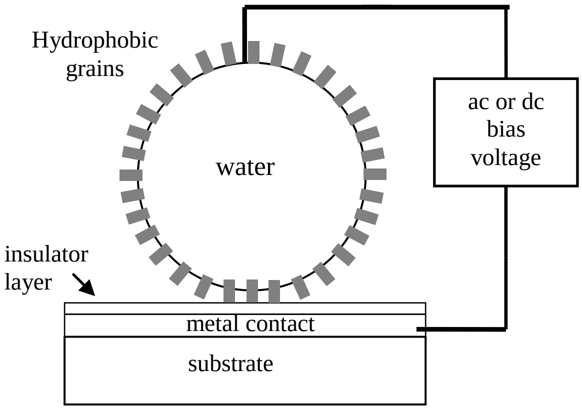
Figures



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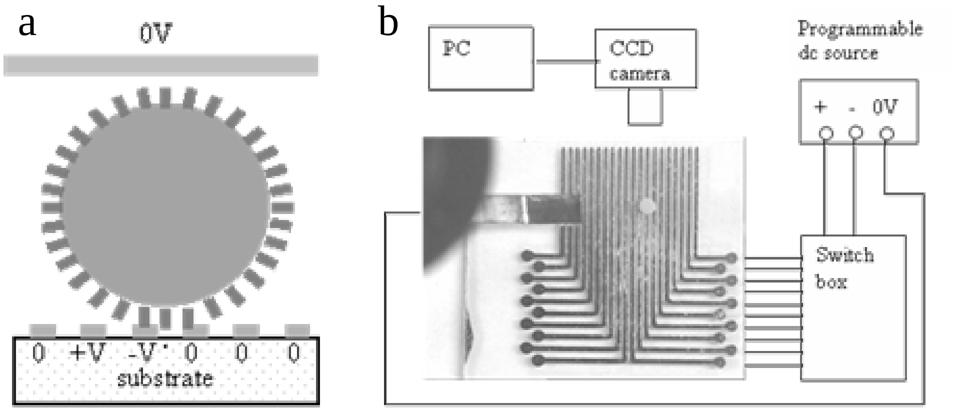

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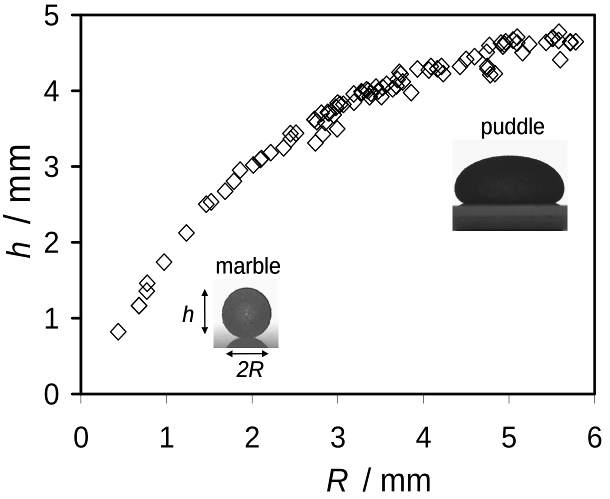

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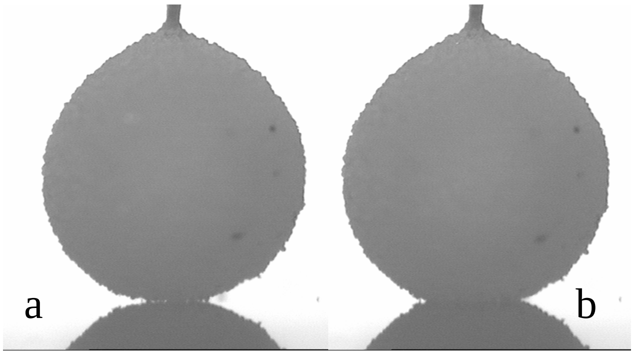

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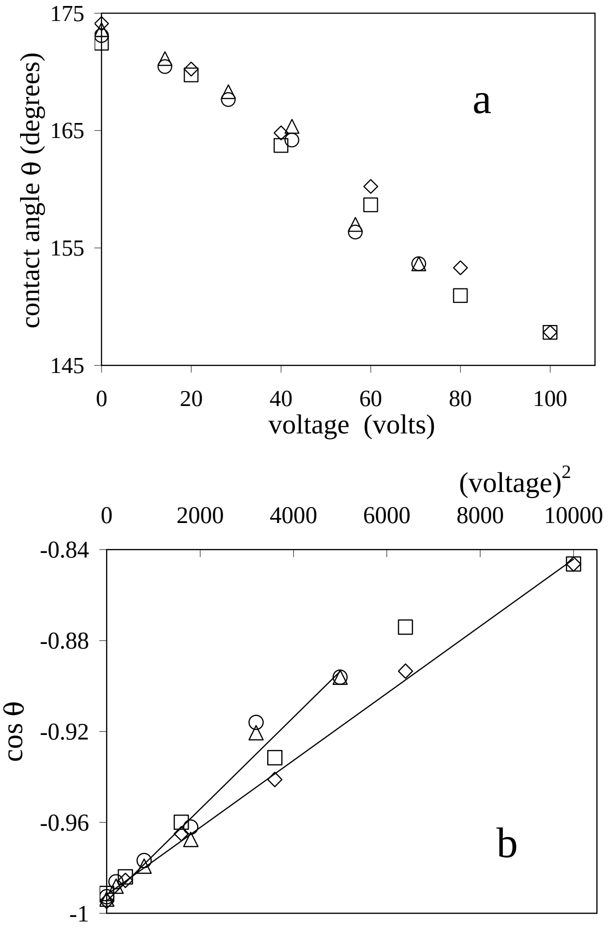

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