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# Investigation of effective interface potentials by electrowetting

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**Abstract.** – We study a situation where the complete wetting of a dielectric solid by a dielectric liquid, in a conducting surrounding, is altered by the application of an electrical potential difference. Calculations predict a dewetting transition towards pseudo-partial wetting. More generally, in a pseudo-partial wetting situation (pre-existing or electrically induced), the mesoscopic film coexisting with the macroscopic droplet is expected to be thinned by the electrostatic pressure in a way that is directly related to its effective interface potential. This points out a possibility to tune the thickness of a fluid film in a nanometric regime.

*Introduction.* – The recent development of integrated microfluidic systems points out the importance of liquid actuation, and numerous physical phenomena were investigated these last years to handle liquids at small scales where pressure is prohibitively difficult to control (*e.g.*, dielectrophoresis [1–4] or electro-osmosis [5]). Of particular diversity, and despite possible fading of efficiency due to unavoidable contact angle hysteresis, are effects related to surface forces (asymmetrical texturation [6], thermocapillarity [7], photo- or electro-chemical modification [8, 9] etc., most often combined with surface patterning [10–12]). Amongst those, electrowetting, which is a way of altering the wetting properties of a substrate through the bringing-in of free electrical charges [13], knows some success due to reproducibility and tuning capacities [14–16]. Electrowetting increases the spreading of (conducting) water droplets on hydrophobic substrates, however without allowing to reach complete wetting due to saturation features [17–19]. Motivated by recent experiments consistent with an amazingly weak contact angle hysteresis [14], we are interested in the apparently symmetrical situation, where the wetting of a (dielectric) oil droplet in a water environment is reduced when charges are brought through water [14, 20]. In such a configuration, "electro-dewetting" of an initially complete wetting situation is discussed here when long-range forces are taken into account.

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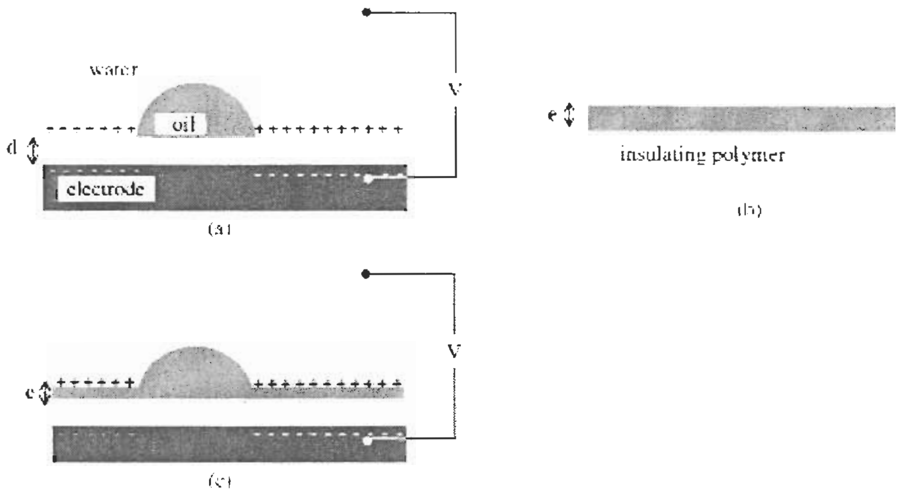

Fig. 1 – (a) Partial wetting situation of a dielectric liquid ("oil") in an environment of conducting liquid ("water") on an insulator surface ("polymer") (here with a potential difference imposed between water and an electrode placed under the insulating polymer). (b) Complete wetting situation. In cases when the spreading is not limited by geometrical factors, the equilibrium thickness was calculated in ref. [23]. (c) Electrically induced dewetting towards a pseudo-partial wetting situation.

*Model.* – The situation under study concerns the wetting of a dielectric liquid on a solid insulator, in a conducting liquid environment. In accordance with previous work on electrowetting, we will designate the present elements by the terms of oil, polymer and water, and we suppose that the two fluids are perfectly immiscible. Let us first recall what happens for oil that partially wets the polymer against water (*i.e.* with a finite contact angle $\theta_0$), when a potential difference $V$ is imposed between the conducting water and an electrode placed under the insulating polymer (fig. 1a). As in usual electrowetting experiments, the resulting condensator just tends to lower its free energy by increasing its capacity, which depends on the spatial repartition between conducting and non-conducting fluids. For the particular case of oil-in-water electrowetting, which is the subject of discussion here, previously published experiments [14,20] showed that oil droplets make with the insulating polymer a contact angle $\theta$ whose dependence on $V$ can be written, through a slight adaptation of the now classical water-in-air electrowetting formula [21], as

$$\cos\theta = \cos\theta_0 - \frac{C_0 V^2}{2\gamma_{\mathrm{ow}}}, \tag{1}$$

where $C_0$ refers to the polymer capacitance (capacity per unit surface).

Let us now discuss the case where oil totally wets the polymer against water (fig. 1b). As this wetting state is to be modified by the electrical potential difference between water and polymer, we can expect a dewetting transition towards a partial wetting state as described above. In order to determine the main features of this transition, we will use a continuum description to study the energy of an oil film of thickness $e$, sandwiched between polymer and water. In the absence of any electric field the oil film free energy per surface unit would write

$$F_0(e) = \gamma_{\mathrm{so}} + \gamma_{\mathrm{ow}} + P(e), \tag{2}$$

where $\gamma_{\mathrm{so}}$ and $\gamma_{\mathrm{ow}}$ (respectively, solid(polymer)/oil and oil/water bare interfacial energies) are due to short-range forces, and $P(e)$ is the interaction free energy per surface unit, or effective interface potential [22]. One limit case is $e = 0$, that corresponds to a simple polymer/water interface without oil (we will call this "dry surface" in the following, the notion of dryness, for this polymer/oil/water system, being of course used by analogy with the usual solid/liquid/gas system). The second limit is $e = \infty$, *i.e.* two extremely separated polymer/oil and oil/water interfaces. If this latter is the reference state ($P(\infty) = 0$), then [23] $P(0)$ is equal to the initial spreading parameter [24] defined by $S = \gamma_{\mathrm{sw}} - \gamma_{\mathrm{so}} - \gamma_{\mathrm{ow}}$, where $\gamma_{\mathrm{sw}}$ is the polymer/water bare interfacial energy. For the complete wetting systems we are dealing with, $S$ is positive. Within these limits, there is no general description of $P(e)$ from molecular to macroscopic scale, but qualitative features are acknowledged according to the range of $e$ that is under consideration. Oscillations are expected at molecular scale due to short-range intermolecular forces and partial solvent ordering [25], while for distances larger than nanometric recent experiments were consistent with a repulsive part in $1/e^8$ [22] or $1/e^3$ [26,27]. The range of $e$ corresponding to both behaviours is here globally gathered under the term "microscopic". With increasing $e$, the main contribution to the effective interface potential are long-range van der Waals interactions. For $e$ smaller than a characteristic ultraviolet absorption wavelength $\lambda$ (range to which we will reserve the term of "mesoscopic scale"), nonretarded van der Waals interactions express as $P(e) = A/12\pi e^2$, where $A$ is the Hamaker constant of water/polymer interactions through oil. The sign of $A$ may be either positive (repulsive interactions) or negative (attractive interactions) [25]. For $e > \lambda$, $P(e)$ presents a more rapid decay in $1/e^3$ [24,25,28].

As a potential difference $V$ is imposed between water and the electrode below it, the electrostatic contribution has to be taken into account in the free energy. For classical electrowetting without oil film (eq. (1)), the corresponding term was $-(1/2)C_0V^2$. Here, polymer and oil layers form two capacitors in series, of total capacitance $C_0/(1 + \varepsilon_{\mathrm{p}}e/\varepsilon d)$, where $d$ is the uniform and constant polymer thickness, and $\varepsilon$ and $\varepsilon_{\mathrm{p}}$ are, respectively, the dielectric permittivities of oil and polymer. The film surface energy then writes

$$F_v(e) = F_0(e) - (1/2)C_0V^2/(1 + \varepsilon_{\mathrm{p}}e/\varepsilon d). \tag{3}$$

For large values of $e$ the concave electrostatic term is predominant, leading to an instability of the film towards spinodal decomposition (1). We will not discuss here the related feature, since the vicinity of the critical point concerns oil thicknesses much larger than we need (nanometric scale). Far from the continuous transition, calculations may be restricted to $e < \lambda$ without losing significant situations. Then i) van der Waals interactions are nonretarded; ii) the oil layer thickness $e$ is negligible compared to the polymer thickness $d$ (orders of magnitude are provided in the following); the electrostatic term may then be linearized in $e/d$:

$$F_v(e) \approx \gamma_{\mathrm{so}} + \gamma_{\mathrm{ow}} + A/12\pi e^2 - (1/2)C_0V^2(1 - \varepsilon_{\mathrm{p}}e/\varepsilon d). \tag{4}$$

Minimization of $F_v(e)$ determines the equilibrium situation of a large drop; it appears at once that the qualitative location of the minimum (microscopic or mesoscopic scale) depends on a great extent on the sign of $A$.

*Repulsive interactions (case $A > 0$).* – The electrostatic term, being monotonically increasing with the oil thickness $e$ for non-zero values of $V$, induces an energy minimum at a mesoscopic scale, where $P(e) = A/12\pi e^2$ (fig. 2), for a thickness

$$e_1 = \left(\frac{\varepsilon_0\varepsilon A}{3\pi C_0^2V^2}\right)^{1/3}. \tag{5}$$

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(1) For example, with $A > 0$ and the orders of magnitude proposed in the next section, we expect instability over $\sim 400\,\mathrm{nm}$ (inflexion point of $F_v(e)$).

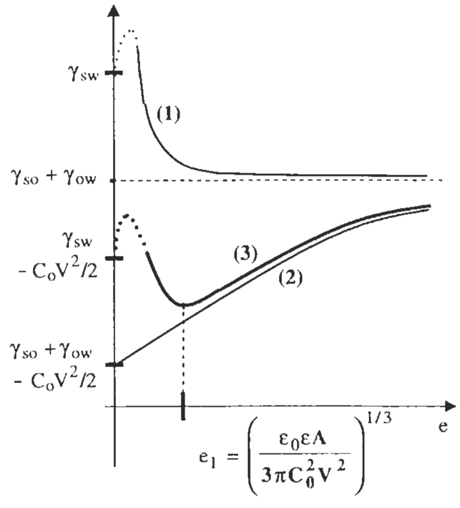

Fig. 2 – Schematic curves of the energies *vs.* the oil layer thickness $e$. (1) $F_0(e) = \gamma_{so} + \gamma_{ow} + P(e)$. Full line: $P(e) = A/12\pi e^2$ (mesoscopic scale). Dashed line: microscopic scale, for which possible occurrences of minima are discussed in the text. Here $P(e)$ is supposed continuous, hence the $\gamma_{sw} = S+(\gamma_{so}+\gamma_{ow})$ limit at $e = 0$. (2) Modification of the short-range interfacial energies due to electrostatic contribution, *i.e.* $\gamma_{so}+\gamma_{ow}-(1/2)C_0V^2(1-\varepsilon_p e/\varepsilon d)$. For small values of $e$, the slope is $\frac{C_0V^2}{2\varepsilon_0\varepsilon}$. (3) Total free energy per surface unit $F_v(e)$. Please note that these curves are only schematic and enhance the trough deepness, whose stability is discussed in the third section.

Using values typical for electrowetting experiments ($\varepsilon = 4$, $A = 10^{-20}\,\mathrm{J}$, $C_0 = 10^{-6}\,\mathrm{F/m^2}$, $V = 50\,\mathrm{V}$), the order of magnitude of this minimum is $e_1 \sim 25\,\mathrm{nm}$, which is below $\lambda \sim 400\,\mathrm{nm}$ and much smaller than the insulator thickness $d$ of order $\varepsilon_0/C_0 \sim 10\,\mu\mathrm{m}$, justifying *a posteriori* the two approximations of eq. (3) [29].

If $P(e)$ at microscopic scales is sufficiently high not to induce a different absolute minimum in $F_v(e)$ (the consequences of the contrary occurrence are discussed later), one can expect a situation where a thin film of thickness $e_1$ is in equilibrium with a macroscopic drop, acting as a reservoir (fig. 1c). This situation, referred to as *pseudopartial wetting* in ref. [23], and as *frustrated-complete wetting* in ref. [30], was predicted and observed in bare systems (*i.e.* $V = 0$), for attractive long-range forces ($A < 0$) [23,31,32] and for repulsive ones [33]. Vanishing of a negative Hamaker constant with temperature provided the first experimental occurrence of a 2nd-order, or critical, wetting transition [26,27]; we expect the voltage difference to induce the same kind of transition. In the model presented here, increasing of $V$ makes the minimum $e_1$ vary continuously from macroscopic to microscopic values, allowing the occurrence of a 2nd-order wetting transition between total and pseudo-partial wetting in a long-range repulsive system. From an experimental point of view, the thickness $e$ of the microscopic oil film depends on i) the Hamaker constant $A$ of water-polymer interactions through oil; ii) the controlled potential difference $V$; and iii) other fully determined parameters (dielectric constants, polymer thickness etc.): $A$ could then be quite straightforwardly determined by measurement of $e$ (*e.g.*, by ellipsometry). Moreover, it is worth noting that by using Young's equation with $F_v(e)$ as an effective solid/water interfacial energy, one gets a new equation for electrowetting:

$$\cos\theta = 1 + kV^{4/3} - \frac{C_0V^2}{2\gamma_{ow}}, \qquad \text{with} \qquad k = \frac{1}{4\gamma_{ow}}\left(\frac{C_0^4 A}{3\pi(\varepsilon_0\varepsilon)^2}\right)^{1/3}. \tag{6}$$

However, the second term, in $V^{4/3}$, is negligible for typical orders of magnitude. Ideal electrowetting experiments (= at equilibrium) should then show a linear dependance of $\cos\theta$ *vs.* $V^2$, with $\cos\theta = 1$ (total wetting) only for $V = 0$:

$$\cos\theta = 1 - \frac{C_0 V^2}{2\gamma_{\mathrm{ow}}}. \tag{7}$$

*Film stability and behaviour for higher oil thicknesses.* – Let us now evaluate the stability of the microscopic film electrically created towards thermal fluctuations. Spatial variations of the interface position from its flat equilibrium position are described by $u(x,y) = u(\vec{\rho})$. The total free energy of the system then writes

$$\mathcal{F} = \int\!\!\int F_v(e + u(x,y))\,\mathrm{d}x\,\mathrm{d}y.$$

In a harmonic approximation, and for slowly varying fluctuations, this can be expressed as

$$\mathcal{F} = \mathcal{F}_0 + \int\!\!\int F_v''(e_1)u^2 + \frac{1}{2}\gamma_{\mathrm{ow}}\left(\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2\right)\mathrm{d}x\,\mathrm{d}y,$$

where $\mathcal{F}_0$ represents the system free energy at the $F_v$ minimum $e_1$. Through Fourier transform and equipartition theorem [34], we obtain the mean-square value of each Fourier mode:

$$\langle |u(\vec{q})|^2\rangle = \frac{kT}{\gamma_{\mathrm{ow}}(q^2 + \xi^{-2})},$$

with $\xi = \sqrt{\frac{\gamma}{2F_v''(e_1)}}$. Thermal fluctuations with a wave vector smaller than $\xi^{-1}$ are cut off by the potential trough in $F_v$. As $\xi < 1\,\mathrm{mm}$ as soon as $V > 1\,\mathrm{V}$, $\xi$ is small compared to the lateral film extension $\sqrt{\Sigma}$ (whose reasonable order of magnitude is the centimeter), and this cut-off is effective. Mean-squared fluctuations then write $\langle |u(\vec{\rho})|^2\rangle = \frac{kT}{2\pi\gamma_{\mathrm{ow}}}\,\mathrm{Ln}\,\frac{\xi}{a}$ ($a$ being a molecular size), which provides a typical thickness fluctuation $l = \sqrt{\langle |u(\vec{\rho})|^2\rangle}$ that does not exceed 5 Å. These fluctuations are negligible compared to the film thickness; we are then in a situation of high enough surface tension to prevent the film from being perturbed by thermal fluctuations.

*Microscopic dewetting.* – The preceding calculation showed that critical dewetting transition may be electrically induced from complete wetting, towards a pseudo-partial wetting state in which macroscopically dewetted surfaces are covered with a stable microscopic film. One can wonder whether a "complete" dewetting (*i.e.* towards a partial wetting state, without oil film on the macroscopically dewetted areas) may be reached at higher voltages. This could only be the case if, by increasing $V$, the film free energy per surface unit $F_v(e)$ would present an absolute minimum in $e = 0$. In fact, we can calculate that for voltages such that $e_1(V) > \sqrt{\frac{A}{8\pi S}}$, $F_v(0) = \gamma_{\mathrm{sw}} - C_0V^2/2$ remains higher than the minimum value of $F_v(e)$ in the mesoscopic scale (reminding that we designate by this term the region where the $1/e^2$-dependence of $P(e)$ is valid, approximately down to 5 nm and up to 300 V, and then $F_v(e)$ is minimum for $e_1$ determined by eq. (5)). Since the limit thickness $\sqrt{\frac{A}{8\pi S}}$ is of order 2 Å for a typical spreading parameter $S = 10^{-2}\,\mathrm{N/m}$, transitions towards a dry state are unlikely to happen in the mesoscopic regime. It could happen for higher values of $V$, *i.e.* from microscopic oil thicknesses, but we will not discuss this occurrence any further, as quantitative predictions would need a more precise knowledge of $P(e)$ in the microscopic scales. The important point is that performing electrowetting on an oil that wets completely a solid against water is a sufficient condition to obtain easily a situation where an oil droplet wets with a finite contact angle a *liquid* surface (polymer + nanometric oil film). As liquid surfaces present much less heterogeneities than solid ones, this result could explain the very low hysteresis observed in variable focal lens devices [14], and more generally suggests experimental clues for studying wetting hysteresis.

*More generally.* – Whatever the behaviour at mesoscopic scales (attractive or repulsive van der Waals interactions), another interesting case in the discussion concerns situations where the effective interface potential $P(e)$, and then the free energy without electric field $F_0(e)$, presents an absolute minimum for some microscopic value $e_{\text{min}}(V=0)$ (which is, for example, expected to happen in a continuum picture when $A<0$ and $S \geq 0$ [23]). When $V$ increases from 0, this minimum is displaced towards smaller thicknesses due to the addition of an electrostatic term whose slope increases with $V$. From the approximate form of $F_v(e)$ (eq. (3)), still valid here, the value of this latter is $\frac{C_0 V^2}{2\varepsilon_0\varepsilon}$. In $e_{\text{min}}(V)$, minimum of $F_v(e)$, this slope is counterbalanced by the one of the effective interface potential $P(e)$; this implies

$$P'(e_{\text{min}}(V)) = -\frac{C_0 V^2}{2\varepsilon_0\varepsilon}.$$

As the second term depends only on accessible parameters, this relation renders conceivable an experimental determination of $P'(e)$ for $e < e_{\text{min}}(0)$, by varying $V$ and measuring the oil layer thickness $e = e_{\text{min}}(V)$. The interface potential $P(e)$ is then to be rebuilt from $P'(e)$, in a microscopic region that is much less systematically known than at the mesoscopic scale.

*Conclusion.* – Calculations of this letter show that very easy electrowetting-like experiments on well-chosen polymer/brine/oil systems are likely to lead to a situation where a mesoscopic or microscopic film, submitted to an electrostatic pressure, is in equilibrium between a polymer substrate and water. Both stress (the electrostatic pressure) and "strain" (its effect on the film) are obtainable from experimental values $V$ and $e$; and their log-on should provide indications on the interactions that underlie the system: Hamaker constant for mesoscopic films, or interface potential at lower scales. In its principle, this recalls what happens in surface-force apparatuses, with the interesting difference that stress is obtained through a non-mechanical set-up. We expect that the ideas presented here constitute the basis for a new way to explore complex dielectric liquids at scales typical of soft-matter interactions.

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