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Effect of submicron particles on electrowetting on dielectrics (EWOD) of sessile droplets

Debapriya Chakraborty [a], Gogineni Sai Sudha [b], Suman Chakraborty [a], Sunando DasGupta [b,*]

[a] Department of Mechanical Engineering, Indian Institute of Technology, Kharagpur 721 302, India
[b] Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721 302, India

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ABSTRACT

The present study elucidates the effects of included submicron-sized particles on the wetting behavior of sessile droplets under the influence of applied electric field in an electro-wetting-on-dielectric (EWOD) configuration. A thermodynamic description using an energy minimization approach is used to analyze the experimental results related to the effects of the included particles on the EWOD phenomenon, considering the effects of line tension as well. The effects of particle size and concentration on interfacial areas are included in the model to analyze the wetting characteristics. Experiments are also conducted with submicron-sizes latex beads, in an effort to elucidate the related phenomena. It is further postulated that these beads act as suspended dielectrics in the droplet, thereby mimicking a system of two capacitors in series. An effective electrical permittivity of the composite medium is used to study the experimental results related to contact angle changes at different concentrations and diameters of submicron particles in the droplet.

1. Introduction

Rapid developments in the field of biomedical, bio-technological and micro-electronics applications have resulted in extensive use of droplet based systems in miniaturized fluidic applications, commonly known as *Digital Microfluidics* [1,2]. Such micro-scale systems are often characterized by the presence of solid–liquid–vapor triple junctions [3] and the motion of the contact line formed by two immiscible fluids and the solid boundary. The shape of a liquid droplet on a surface is determined by a delicate balance between the solid–liquid, liquid–vapor and solid–vapor interfacial tensions present in the three phase contact line, morphology of the underlying solid surface, and the volume and composition of the liquid at equilibrium [4]. The contact angle, defined as the local tangent at the junction of three phase contact line, is the commonly observable parameter governing the drop shape which is an implicit indicator of the wettability and nature of the substrate with respect to the liquid. Local modulation of contact angle provides a flexible means of flow actuation catering to the needs of several microfluidic systems, where the favored scaling [5] of the surface forces in comparison to the other body forces over reduced length scales plays a pivotal role. Different methods like electrical, chemical [6], thermal [7], electrochemical [8], and photochemical [9] have been used to alter the contact angle of the three phase contact line. The electrical method probably is the most promising one for lab-on-a-chip based microfluidic applications, offering the promise of high energy efficient and inherently integrable compact electromechanical systems.

On application of an electrical potential, the interfacial tension gets modified which leads to an asymmetric deformation of the meniscus at the two ends and thus a motion of droplet can be actuated. The principle of altering the wetting properties of fluid by modifying the interfacial tension of the contact line with the application of electric potential is commonly known as electrowetting [10]. However, electrochemical reaction between the electrode and the aqueous medium, leading to current flow from the substrate to the solution, restricts the application of higher voltages. In order to avoid such undesirable reactions, the liquid and the electrodes are separated by a thin dielectric layer and such a configuration is commonly known as electrowetting on dielectric or EWOD [11–21]. The dielectric serves both to block the electron transfer and also to provide a hydrophobic surface that enables large changes in contact angle. The change in contact angle is a function of the thickness and permittivity of the dielectric.

Fluid elements with particle inclusion, mostly nano-scale particles in suspended forms (also known as nanofluids), have been studied in the literature, with a motivation of achieving high transport coefficients as well as imposing tuneable controllability on the resultant interfacial phenomena. Interestingly, the well-established concepts of spreading and adhesion of simple liquids do not apply to fluids containing particles of nanometer dimensions [22]. A solid-like ordering of suspended spheres occurs in the confined

* Corresponding author.
E-mail address: sunando.dasgupta@gmail.com (S. DasGupta).

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three-phase contact region at the edge of the spreading fluid, which tends to become more disordered and fluid-like towards the bulk phase. The pressure arising from such colloidal ordering in the confined region also enhances the spreading behavior of nanofluids. On the contrary, the behavior for non-wetting fluids with suspended particles has not been extensively studied till date. There are a few investigations about the interfacial effects during evaporation of the droplet of nanofluids. The presence of nanoparticles leads to a reduction in the evaporation rate compared to a simple fluid. The deposition of nanoparticles into the triple contact line wedge during evaporation causes a greater pinning of the nanofluid droplets [23]. The contact angle of a sessile droplet has been found to be decreasing with decrease in the particles size [24]. Apart from the size, concentration also plays an important on the contact angle. Nanoparticles of smaller size leads to larger changes in contact angle at the same mass concentration [25]. EWOD has been studied for nanofluid comprised of an aqueous suspension of bismuth telluride nanoparticles capped with thioglycolic acid (TGA) [26]. Nanofluid droplets have been observed to exhibit enhanced stability with the absence of contact angle saturation. Surface tension lowering and behavior of the particles has been studied for colloidal particle suspension near the interface [27,28]. However, no study has yet been reported in the literature on the explanation of the fundamental interfacial phenomena, including the contact line thermodynamics, associated with the incorporation of submicron-sized particles in a sessile droplet in EWOD configuration.

In the present work, the variation of contact angle of droplets containing submicron-sized particles under the influence of applied electric field in EWOD configuration is investigated. Motivation behind this study stems from the transport of biological macromolecules like suspended cells, coated submicron beads and DNA fragments. The effects of droplet based cell manipulation [29] have been studied for cell vitality and cytotoxicity assay by EWOD which has been proven to be more sensitive than the macroscale methods. The sizes of these cells are typically in the micron or submicron range, altering the characteristics of conventional EWOD. In another context, bead based immunosorbent assay systems have been developed with human secretory immunoglobulin A (s-IgA) adsorbed on the bead surface for reaction with colloidal gold conjugated anti-s-IgA antibody [30]. Such bead based assays using droplet, in contrast to the continuous flow, have proven to be highly specific and efficient from economic perspectives. Keeping such significant implications in view, here we explore the changes in contact angle for a droplet containing submicron particles under the effect of electric fields. However, unlike previous studies in this area, the effects of varying concentrations and diameters of the suspended particles are addressed herein. Conventionally, the suspended nanoparticles contribute only to the increase of the effective electrical permittivity and thermal conductivity. However, in the present context, we have studied the effects of applied potential on the three phase contact line of a droplet in presence of submicron particles. A thermodynamic description using an energy minimization approach is developed to analyze the experimental results. The effects of line tension and modified interfacial areas due to the submicron particles are included in the model. The theoretical trends are consistent with the experimental results and the significance of the model parameters is established. It is postulated that the submicron spherical latex beads act as suspended dielectric in the droplet thereby mimicking a system of two capacitors in series. An effective electrical permittivity of the composite medium is used to examine the voltage drop across the insulating layer and the submicron particles and utilized to analyze contact angle changes and its saturation at varying concentrations and sizes of the suspended particles.

2. Materials and methods

Glass slides were cleaned in Piranha solution (1:1 H_2O_2:H_2SO_4) for 5 min, rinsed in DI water and dried using nitrogen gas jet. These cleaned slides were used to coat gold to serve as one of the electrodes for the EWOD configuration. Chrome was deposited over the glass substrate using a vacuum coating system (Model 12A4-D, HindHiVac, India) which uses evaporation induced coating on substrate to a thickness of 150 nm in order to improve the adhesion of gold. 22 carat gold was deposited in a similar manner over chrome coated glass slide with a thickness of 0.1 μm. Sylgard-184 (a two-part PDMS elastomer; Dow Chemicals, USA) consisting of an oligomer and cross linking agent was used to prepare the dielectric layer by mixing them in 10:1 ratio by weight. The mixed parts were desiccated to eliminate the presence of trapped bubbles while mixing. A small amount of sylgard mixture was poured on the glass substrate for deposition of a thin layer over the glass using a spin coater which was spun at 600 rpm for 10 s for initial ramming, and then gradually increased to 3000 rpm for 60 s. The sylgard coated substrate was cured in an oven at 70 °C for 2 h. The thickness of the deposited film was measured to be 28.3 μm using profilometer (DekTak, Veeco, USA). The Sylgard coated surface was characterized using Atomic Force Microscope to characterize the quality of the coated film (see Supplementary material fig. S1). Submicron polystyrene beads (Sigma–Aldrich, India) of diameters 53 nm, 500 nm and 1 μm were dispersed in DI water at different volume concentrations ranging from 0 to 0.005 and the suspensions were homogenized by ultrasonic agitation for 10 min just before the experiment. The particles are neutral beads (usually hydrophobic surface) obtained in aqueous solutions from the manufacturer. The experiments were performed immediately after ultrasonication to avoid the agglomeration of the particles.

The substrate was placed on a goniometer (Rame Hart, Germany) platform for contact angle measurements as shown in Fig. 1. With the help of a controlled dispenser, a small droplet of the test fluid was placed over the substrate. A platinum electrode was placed at the tip of the droplet and the gold layer acted as the other electrode. Using a DC Sourcemeter, (Model2410 Keithley, USA), voltage ranging from 0–200 V was applied between the droplet and the gold electrode. The change in contact angle was measured, both while increasing as well as decreasing the applied voltage. All the measurements were repeated at least three times and only the average values of the observations are reported here. The standard deviations of the measurements of contact angles are within 1.5%. The contact angle hysteresis observed (i.e., the difference between contact angle measured at the same voltage and particle concentration with increasing and decreasing voltages) is found to be quite small – in the range of the experimental errors. Interestingly, it has been observed that the presence of suspended particles significantly reduces contact angle hysteresis as compared to traditional EWOD experiments without suspended particles. This has recently been reported by other researchers as well [31,32]. However, a physical mechanism leading to the complete understanding of this effect is yet to evolve.

3. Results and discussion

EWOD experiments are performed initially with pure (no suspended particles) DI water as a control. The trends match well with the traditional Young–Lippmann equation:

$$\cos\theta = \cos\theta_0 + \chi V^2 \quad (1)$$

where θ and θ_0 are the contact angles with and without external effects respectively, V is the applied external potential, $\chi = \frac{\varepsilon_0 \varepsilon_r}{2\sigma_{lv} d}$ is the slope of the resulting linear characteristic line of $\cos\theta$ vs. V^2 line,