Capillary Phenomena at Nanoscales: Electrowetting and Capillary Adhesion\textsuperscript{1}

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Theories of capillary phenomena have traditionally been based on continuum approximations that break down as dimensions shrink to nanometer scales. Molecular simulations are used to test the limits of continuum theory in electrowetting on dielectric (EWOD) and capillary adhesion between solids. In EWOD, a fluid drop is separated from an electrode by a dielectric. Increasing the voltage $V$ between drop and electrode, decreases the contact angle $\theta$, allowing the droplet to be manipulated. Simulations of nanoscale drops show the same behavior as experiments on millimeter drops. The contact angle follows the continuum Young-Lippmann equation (YLE) at low voltages and then saturates. The saturation mechanism has been difficult to identify in experiments. Simulations show that charged molecules are pulled from the drop by large electrostatic forces near the contact line. Saturation can be delayed by increasing molecular binding, lowering temperature or increasing dielectric constant. A local force balance equation is derived that agrees with the YLE below saturation and remains valid after saturation. Simulations of capillary adhesion examined the force between a spherical tip of radius $R$ and a flat substrate. The shape of the meniscus agrees remarkably well with continuum theory down to nanometer separations, as does the adhesive force from interfacial tension. However, the total force may deviate by factors of two or have the opposite sign. While the component of the pressure along the substrate agrees with the Laplace pressure from continuum theory, the out-of-plane component does not. There may also be significant force oscillations associated with layering near the solids. The elastic response of the solid has little affect on adhesive forces.

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