Spreading of Electrolyte Drops on Charged Surfaces: Electric Double Layer Effects on Drop Dynamics

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Abstract

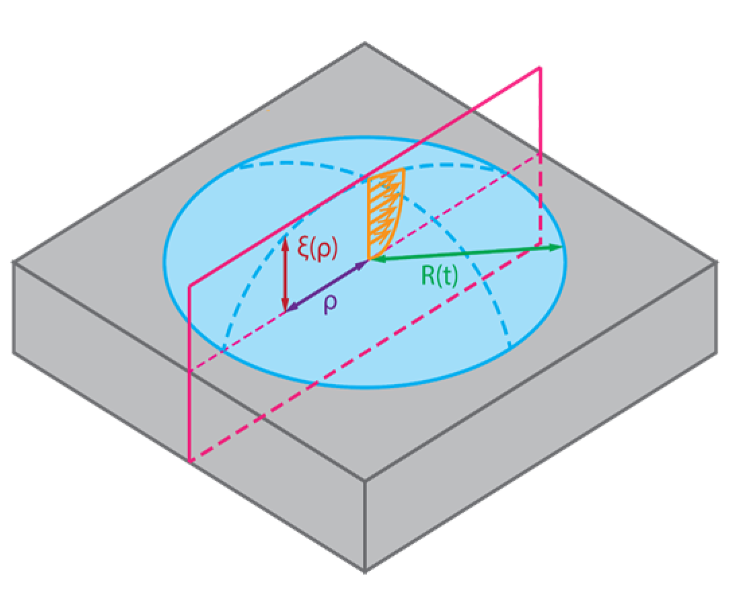
The phenomenon of drop spreading on various surfaces have been widely studied previously. In this paper we propose a theory for drop spreading on charged surfaces. Initially the sessile liquid droplet is placed on a charged solid surface in a non-equilibrium condition. The time evolution of the contact angle and the increase in the base radius have been studied. We have used an energy approach towards the study of this mechanically dissipative system. We show that the free-energy change for a spreading drop at various time instants on a charged surface is lesser than that of an uncharged surface. This quantifies the fact that the drop spreads much faster on a charged surface than a normal uncharged surface. We consider the initial contact angles of several substrates and use them for the parametric study. We believe that that this thorough study will open new directions in drop dynamics over charged systems through the contribution of Electric Double Layer (EDL).

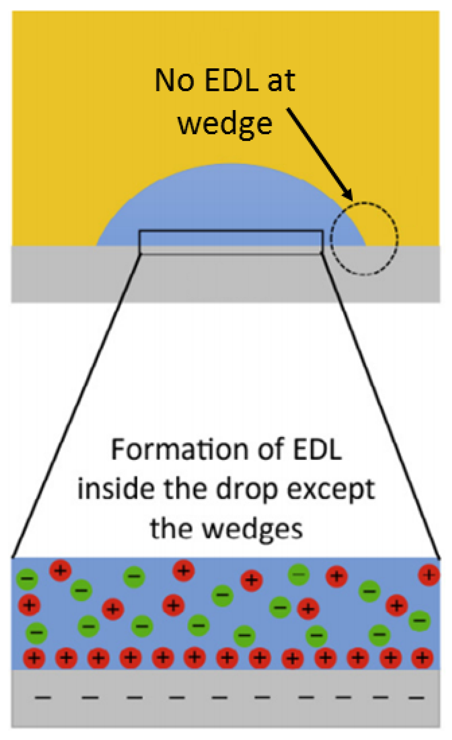
Introduction

Applications

Drop spreading is a widely observable phenomenon around us. It has huge applications in the fields of coating, painting and gluing of surfaces. It can also be used for recovery of crude oil from porous rock beds, lubrication purposes of engineering machinery etc. The liquid is in the form of an oil as for the later cases of lubrication. In this problem we consider a water droplet spreading on a charged rigid substrate. The surface considered has some initial charges.

Schematics





Theory

Assumptions: the liquid drop always forms a spherical cap, and neglect the pre-cursor film that invariably precedes the contact line during the spreading. R is the base radius, V is the volume.

$$\frac{R^{3(t)}}{V} = \frac{3}{\pi}\phi[\theta(t)]$$

$$\phi[\theta(t)] = \frac{[1+\cos\theta(t)]\sin\theta(t)}{[1-\cos\theta(t)\,][2+\cos\theta(t)\,]}$$

The corresponding height at the apex of the droplet can be expressed as:

$$h(t) = R(t)\frac{1-\cos\theta(t)}{\sin\theta(t)}$$

The free energy of this drop can be expressed as:

$$F\{R(t)\} = \pi R^2(\gamma'_{SL} - \gamma_{SG}) + 2\pi\gamma\int_0^{R(t)} \rho\sqrt{1+\left(\frac{d\xi(\rho)}{d\rho}\right)^2}\,d\rho$$

Where $\gamma'_{SL} = \gamma_{SL} + W_{EDL}$ and W_{EDL} is the per unit area electrostatic free energy due to the EDL, $W_{EDL} < 0$

$$cos\theta'_{eq} = \frac{\gamma_{SV} - \gamma'_{SL}}{\gamma} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma} - \frac{W_{EDL}}{\gamma} = cos\theta_{eq} - \frac{W_{EDL}}{\gamma}$$

Here θ_{eq} is the equilibrium contact angle, whereas θ'_{eq} is the modified equilibrium contact angle due to EDL effects. we can finally quantify the drop spreading behavior by expressing the rate of change of drop base radius, $\dot{R}(t)$

$$\dot{R}(t) = \frac{\gamma[\cos\theta_{eq} - \cos\theta(t)] - W_{EDL}}{\zeta_0 + 6\eta\phi[\theta(t)]\ln\left[\frac{R(t)}{a}\right]}$$

where a is the lower cut-off of the value ρ and ζ_0 is the friction coefficient expressed as:

$$\zeta_0 = \frac{nk_BT}{K_w^0\lambda}$$

where k_BT is the thermal energy, n is the concentration of the adsorption sites (see 2 for details) and Kw and λ are the typical jump frequency and length of molecular displacements.

Dimensionless parameters:

$$\bar{R} = \frac{R}{R_0}, \bar{t} = \frac{t}{t_0}, where\ R_0 = V^{\frac{1}{3}}, t_0 = \frac{\eta R_0}{\gamma}$$

$$\frac{d\bar{R}(\bar{t})}{d\bar{t}} = \frac{t_0}{R_0}\frac{dR(t)}{dt} = \frac{\cos\theta_{eq} - \cos\theta(\bar{t}) - \frac{W_{EDL}}{\gamma}}{\frac{\zeta_0}{\eta} + 6\phi[\theta(\bar{t})]\ln\left[\frac{R_0}{a}\bar{R}(t)\right]}$$

Substituting $\phi[\theta(\bar{t})]$, we get

$$\bar{R}^3(\bar{t}) = \frac{R^3(\bar{t})}{V} = \frac{3}{\pi}\frac{[1+\cos\theta(t)]\sin\theta(t)}{[1-\cos\theta(t)\,][2+\cos\theta(t)\,]}$$

Taking the first derivative of both sides:

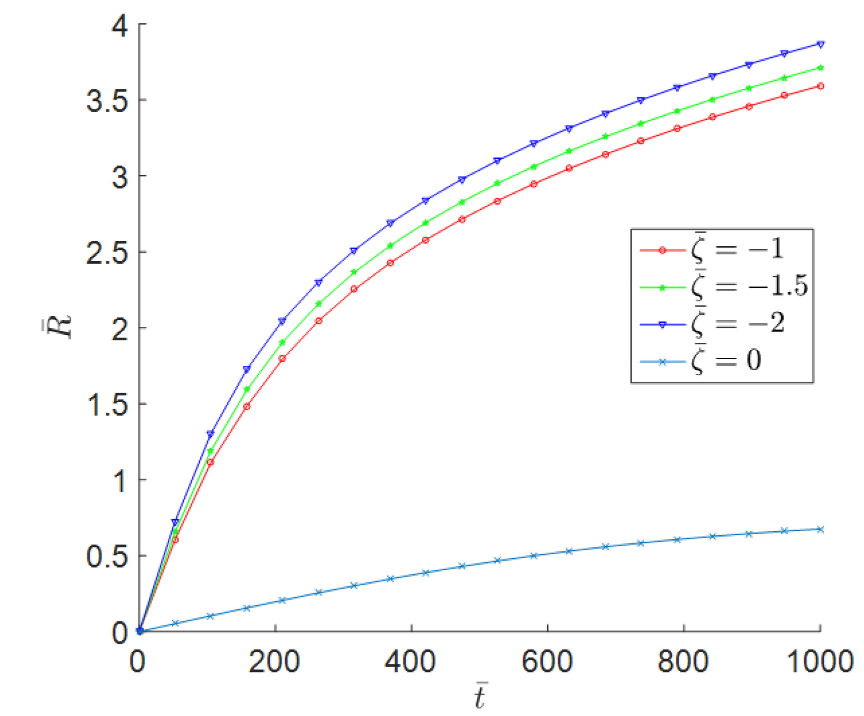
$$\frac{d\bar{R}(\bar{t})}{d\bar{t}} = \frac{1}{\pi\bar{R}^2(\bar{t})}\frac{-3[1+\cos\theta(\bar{t})]}{[1-\cos\theta(\bar{t})][2+\cos\theta(\bar{t})]^2}\frac{d\theta(\bar{t})}{d\bar{t}}$$

Results

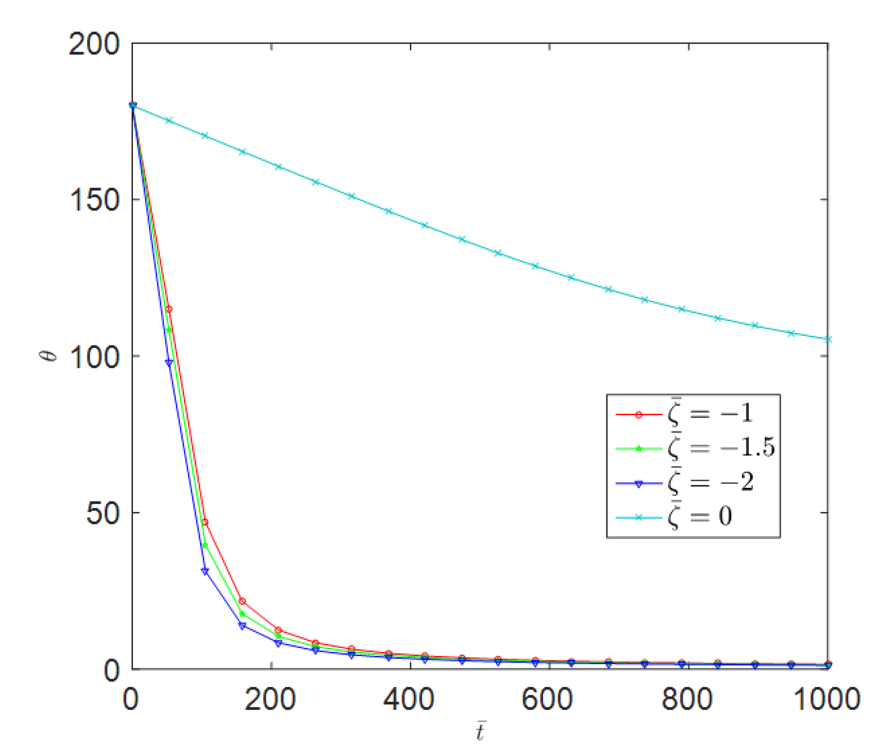
Simplifying to the following:

$$\frac{d\theta(\bar{t})}{d\bar{t}} = \frac{\cos\theta_{eq} - \cos\theta(\bar{t}) - \frac{W_{EDL}}{\gamma}}{\frac{\zeta_0}{\eta} + 6\phi[\theta(\bar{t})]\ln\left[\frac{R_0}{a}\bar{R}(t)\right]}\frac{[1-\cos\theta(\bar{t})][2+\cos\theta(\bar{t})]^2}{-3[1+\cos\theta(\bar{t})]} * (3\sqrt{\pi}\phi[\theta(t)])^{2/3}$$

Solution of R(t)



Solution of θ



$$\bar{\zeta} = \frac{e\zeta}{K_BT}$$

$$\bar{W}_{EDL} = f(\zeta)$$

Discussion

- A drop spreads on a surface due to the action of three components. One is the friction of the substrate that resists the motion of the contact line. The other is the quasi-static Couette flow in the drop that enhances the spreading.
- There is a also a contribution from the formation of a precursor film which we have neglected here.
- The energy of the electric double layer formed on the substrate enhances the flow of the drop which increases it's spreading power.
- We do not consider the presence of EDL at the wedges of the drop that is at the zone of the three phase contact line (TPCL).
- The surface has some pre-acquired charges on it.
- The evolution of the contact radius with respect to time is much faster for a charged surface.
- We do a parametric study for drop spreading on surfaces with different zeta potential.
- The contact angle decreases much faster than the uncharged substrate.
- W_{EDL} being a function of the zeta potential decreases as the zeta potential decrases.
- In future we plan to calculate the zeta potential for various real life substrates and calculate the EDL potentials of them. We will use that for the drop spreading calculations.

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References

1. P. G. de Gennes, Rev. Mod. Phys. 57, 827 (1985).
2. M. J. de Ruijter, J. De Coninck, and G. Oshanin, Langmuir 15, 2209 (1999).
3. M. Manciu and E. Ruckenstein, Langmuir 19, 1114 (2003).
4. S. Das, S. K. Mitra, and S. Chakraborty, Phys. Rev. E 86, 011603 (2012).
5. S. Das, Phys. Rev. E 84, 036303 (2011).
6. S. Das and S. K. Mitra, Phys. Rev. E 88, 033021 (2013)