MICRO-413 (2024) / Inkjet Printing: Exercise 2

1) The wettability of substrates plays a significant role in print quality. A simple method to determine the surface wettability is by measuring the droplet contact angle on the substrate. On a flat and chemically homogenous substrate, the equilibrium contact angle (θ_{eq}) depends on the interfacial tensions (γ) at the solid-liquid (SL), solid-gas (SG), and liquid-gas (LG) interfaces. Young's equation ($\cos\theta_{eq} = (\gamma_{SG} - \gamma_{SL})/\gamma_{LG}$) gives the relation between the interfacial surface tensions.

   a) Describe the wetting behavior of a liquid drop on substrates with different contact angles ($\theta_{eq} < 90$), ($\theta_{eq} = 90$), and ($\theta_{eq} > 90$) based on Young's equation.

      i) (If $\theta_{eq} = 0$ spreading)

      ii) If $0 < \theta_{eq} < 90$ → wetting

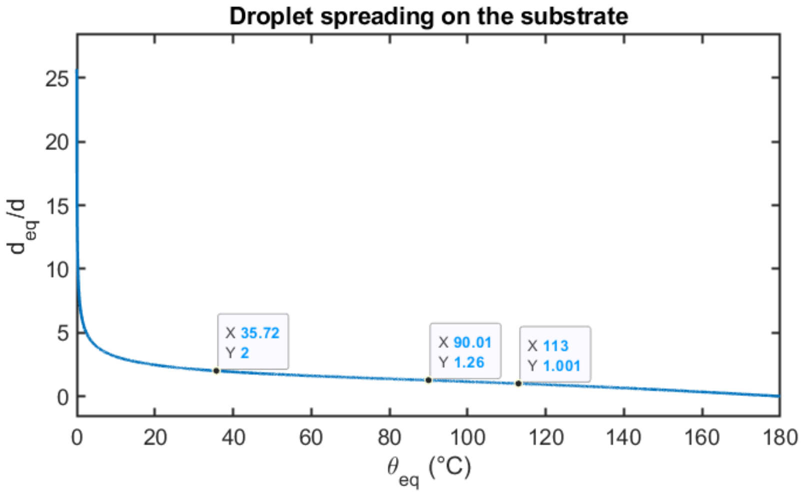
      iii) If $\theta_{eq} = 90$ → partial wetting

      iv) If $90 < \theta_{eq} < 180$ → non-wetting

   b) Assuming that the droplet volume is conserved, how does an inflight droplet's diameter compare with the droplet diameter on the substrate for the three surfaces mentioned above?

   The ratio between the diameter of an inflight droplet (d_0) and the droplet on the substrate at the equilibrium (d_{eq}) depends on the equilibrium contact angle and is calculated using the following equation, given that the droplet volume is conserved:

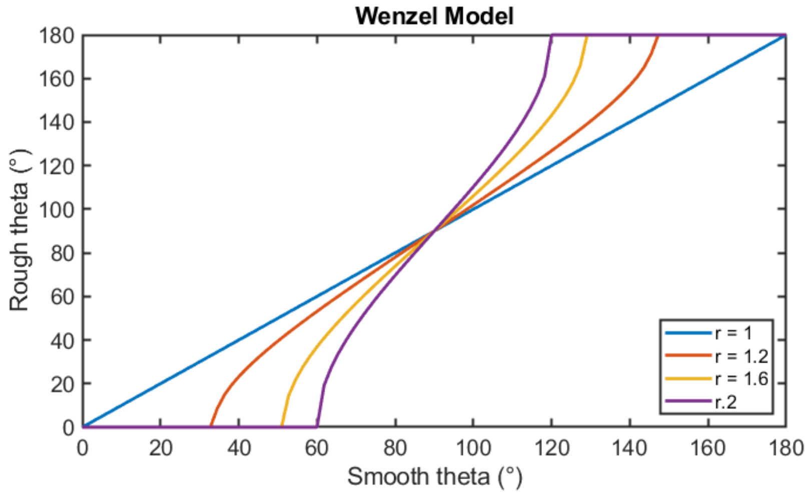
$$\beta = \frac{d_{eq}}{d_0} = \left(\frac{8}{\tan\left(\frac{\theta}{2}\right)\left(3 + \tan^2\left(\frac{\theta}{2}\right)\right)}\right)^3$$



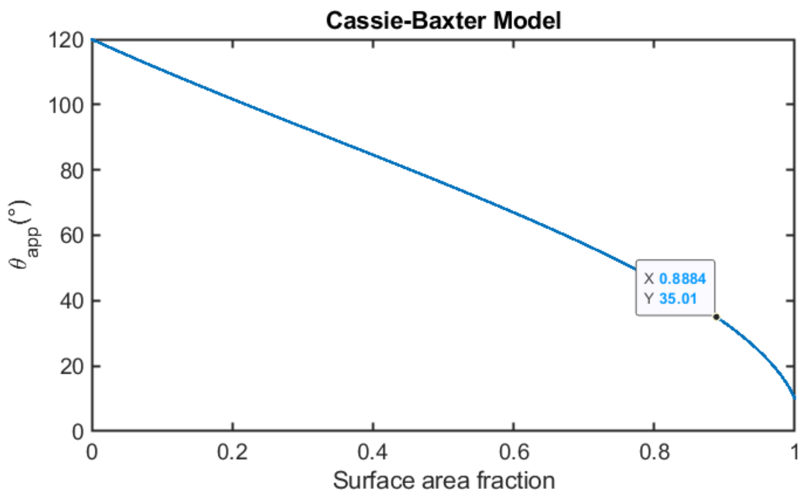
In this equation, β is the spreading factor. As shown in the figure, if the contact angle is less than ca. 36°, the droplet diameter on the substrate becomes more than twice the initial diameter. Further decreasing the contact angle significantly increases d_{eq}. If the contact angle exceeds ca. 113° d_{eq} becomes smaller than d_0.

c) The Wenzel equation ($\cos\theta_{app} = r \cdot \cos\theta_{eq}$) can describe the behavior of a droplet on a rough surface. In this equation r is the roughness factor, and θ_{app} is the apparent contact angle on the rough surface. For surfaces with r values of 1, 1.2, 1.6, and 2, plot the θ_{app} as a function of θ_{eq} in the range of 0 to 180°. Explain the effect of surface roughness on substrate wettability. Schematically show how droplets with equal volumes wet surfaces shown in Fig. 1(a) and (b).

The surface roughness amplifies the wettability of the substrate since, on a rough surface, the read surface area increases. Therefore, a hydrophilic surface becomes more hydrophilic, and a hydrophobic surface becomes more hydrophobic.



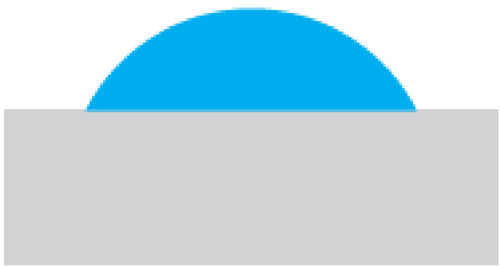
d) On a chemically heterogeneous substrate, the droplet contact angle can be modeled using the Cassie-Baxter equation ($\cos\theta_{app} = \Phi_1 \cdot \cos\theta_1 + \Phi_2 \cdot \cos\theta_2$), where Φ_1 and Φ_2 are the surface area fractions, and θ_1 and θ_2 are the droplet contact angles on each phase. Considering that a water droplet has a contact angle of 10° on the hydrophilic phase and 120° on the hydrophobic phase, calculate the surface areas that lead to the apparent contact angle of 35°.



e) In the previous example, consider a water droplet on a nanostructured substrate where in one case, the hydrophilic and, in the other case, the hydrophobic areas are replaced by grooves. In each case, assuming that the grooves take up 50% of the surface area, calculate the apparent contact angle. Then, explain the difference between the two cases by drawing water droplets with equal volumes on surfaces shown in Fig.1(d) and (e).

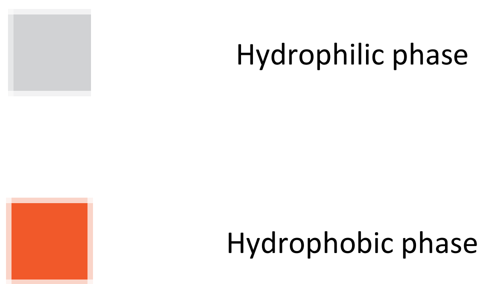
The problem is similar to the Cassie model on the hydrophobic surface, and the droplet behaves as it is on a chemically heterogeneous substrate, where the contact angles are 120° and 180° on the hydrophobic surface and on the air pockets, respectively. Having 50% of each phase results in an equilibrium contact angle of approximately 139°.

On the hydrophilic surface, the water penetrates the grooves, and the droplet is in contact with the asperities of the surface; hence the substrate behaves according to the Wenzel model. In the Wenzel state, the contact angle will be lower compared to the previous Cassie model.


(a)


(b)


(c)



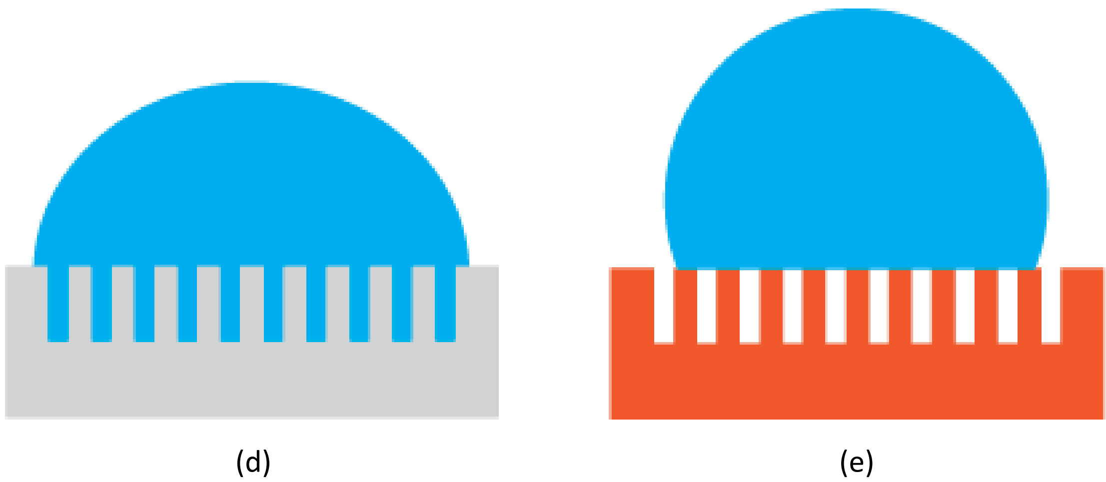


Fig. 1 Substrates with a) chemically homogenous flat surface, b) chemically homogeneous rough surface, c) chemically heterogeneous flat surface, d) hydrophilic surface with nanostructured grooves, e) hydrophobic surface with nanostructured grooves.

2) The morphology of a printed pattern strongly depends on the solvent evaporation mechanism and substrate wettability. To study different evaporation profiles, we study three inks containing 0.1 vol% polystyrene beads dispersed in solvents shown in Table 1

Table 2 Inks containing polystyrene beads

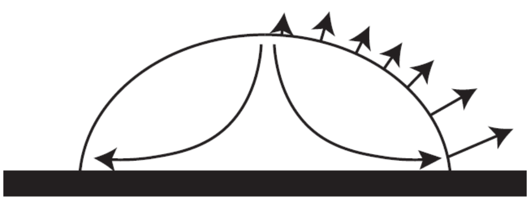
Ink	Water (vol%)	Ethanol (vol%)	Ethylene glycol (vol%)
Ink 1	100	0	0
Ink 2	70	30	0
Ink 3	70	0	30

a) Describe the drying mechanism of sessile droplets printed from the three inks shown in table 1 on a substrate with zero receding contact angle (pinned contact line). Use sketches/drawings to describe the evaporation profile in each case.

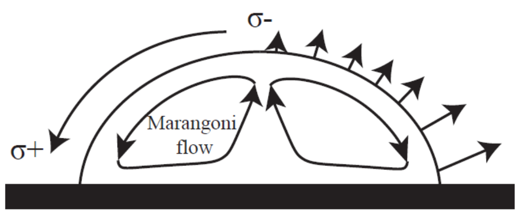
i) Ink 1 contains only water. Evaporation-induced flows inside the droplet carry the PS beads to the contact line and form coffee rings.

ii) Ink 2 contains the water-ethanol solution. Since water has a higher boiling point and surface tension compared to ethanol, the ethanol depletes at the contact line resulting in the surface tension-driven Marangoni flow from the droplet center to the contact line.

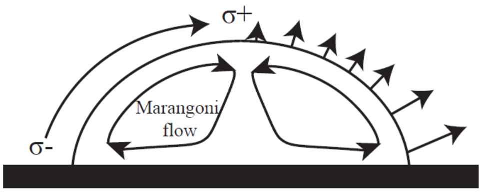
iii) Ink 3 contains water-ethylene glycol. Since water has a lower boiling point but higher surface tension compared to ethylene glycol, the water concentration depletes at the contact line resulting in the surface tension Marangoni flow from the droplet periphery to its center.



Ink 1



Ink 2



Ink 3

b) How does the drying mechanism change if ink 1 is printed onto a substrate with a finite receding contact angle (moving contact line)?

In the case of the fixed contact angle and moving contact line, the particles inside the droplet move towards its center as the solvent evaporates, resulting in a small dot from a larger droplet. Of course, this is the case if the contact line does not get pinned by the particles inside the ink during the evaporation.

Table 3 Relevant physical properties of the solvents

Solvents	Boiling point (°C)	Surface tension at 25°C (mN/m)
Water	100	72.0
Ethylene glycol	197	47.3
Ethanol	78	20.1