Lecture-03-07 Fundamental Concepts Related to Surface and Surface Tension

3.1. Can surface tension be negative?

Ans: No, Surface tension can never be negative, as certain amount of energy is always necessary to create any surface. However, Interfacial tension or can be negative. Dissolution is a physical phenomena that is associated with negative interfacial tension.

3.2. What is "interfacial broadening"? How is it related to miscibility?

Ans: When two different phases are in contact, the intrinsic properties show a gradual transition across the interface and this transition length is known as interfacial broadening. With increase in miscibility, the thickness of the interface and hence the interfacial broadening increases. In the adjoining figure, interfacial broadening is shown by " δ ". Perfect insolubility between two phases would imply $\delta = 0$.



3.3. How is (qualitatively) surface tension of material related to its bond strength?

Ans: Higher is the bond strength, higher energy will be needed to break these bonds and creates a new surface. Hence, it results in higher surface tension of the material.

3.4. What is coordination number and what role does it play in defining surface tension of a material?

Ans: Coordination number of an atom or molecule gives the number of atoms surrounding that atom at a particular location. As the coordination number of any atom on the surface of the material is lesser than that in the bulk, it leads to an inward attraction on the surface manifested as surface tension.

3.5. Why water is a good solvent, as compared to most organic solvents?

Ans: As water has polar component along with van der waals interaction forces, water is a good solvent as compared to organic solvents which lack any polar interactions.

3.6. What are the general properties of hydrophobic and hydrophilic surfaces?

- **Ans:** A hydrophobic surface has lower surface energy and hence lower spreading coefficient. A hydrophilic surface has higher surface energy and spreading coefficient.
- 3.7. Calculate the spreading coefficients when water is dispensed on a polymer surface with surface energy of 39.2 mJ/m². Assume the interfacial tension between the polymer and water to be 1.95 mJ/m². Comment on the stability of the water film.
- Ans: We know that $S = \gamma_S (\gamma_{SL} + \gamma_L)$ On substituting the values of $\gamma_S = 39.2 \text{ mJ/m}^2$, $\gamma_L = 72.8 \text{ mJ/m}^2$ and $\gamma_{SL} = 1.95 \text{ mJ/m}^2$ in the above equation, we obtain $S = -37.75 \text{ mJ/m}^2$ Hence the liquid will partially wet the surface.
- 3.8. A flat surface of a polymer exhibits an equilibrium water contact angle (WCA) of 95°. A grating of the same material is fabricated, where the grating have periodicity of 2.0 μm, line width 1.0 μm and feature height of 300 nm. What is the likely water contact angle on this grating? Also calculate the critical minimum feature height of the patterns, beyond which you would be expecting Cassie state of wetting (substrate periodicity remains unaltered).

If the grating is constructed with a material that exhibits an initial WCA of 85°, what is the expected WCA on the patterned substrate?

Ans: For any surface, the critical roughness at which the wettability regime changes from Wenzel to Cassie is given by the following equation:

$$r_{\rm C} = \frac{-1}{\cos \theta_{\rm E}} \tag{1}$$

In the present case, $\theta_E = 95^\circ$. Thus, $\mathbf{r}_C = 11.473$.

This implies that for the given material, if the surface roughness is less than 11.473, the wetting regime will be Wenzel.

Now for a grating with periodicity of 2.0 μ m, line width 1.0 μ m and feature height of 300 nm, the roughness is $\mathbf{r} = (1000 + 300 + 1000 + 300) / 2000 = 1.3$.

Therefore, on the patterned surface of the above material, the wetting regime is Wenzel type.

Now we know that for wenzel state of wetting, $\cos \theta^* = r \cos \theta_E$ (2)

Substituting r =1.3 and $\theta_{\rm E}$ = 95° in the above equation, we get θ^* = 96.51°.

We know that Cassie state of wetting is possible only when **r** exceeds 11.73. As the substrate periodicity remains unaltered, high roughness can only be achieved when the feature height is higher. Lets say that the feature height is $\mathbf{h}_{\rm F}$. In that case, we have

 $(2000 + 2 h_F) / 2000 = 11.73$

Solving the above equation, we obtain $h_F = 10730$ nm or 10.73 µm.

In case $\theta_E = 85^\circ$, then $\theta^* = 83.49^\circ$ from equation 2 (for r = 1.3).

The result shows that in case of Wenzel State of Wetting, Effective contact angle reduces on a rough surface if θ_E is lower than 90°.

3.9. What is a monopolar surface? Give some example of it.

Ans: Surfaces that only have electron donor properties and no electron acceptor properties are called monopolar surfaces. Monopolar materials manifesting only electron acceptor properties also may exist, but they do not appear to occur in as great abundance. Common electron donor monopolar materials are: polymethylmethacrylate, polyvinylalcohol, polyethyleneglycol, proteins etc. Monopolar materials manifesting only electron acceptor properties also may exist, but they are not available in abundance.

It is worth adding that strongly monopolar materials of the same sign repel each other when immersed or dissolved in water or other polar liquids. The interfacial tension between strongly monopolar surfaces and water has a negative value. This leads to a tendency for water to penetrate between facing surfaces of a monopolar substance and hence, to repulsion between the molecules or particles of such a monopolar material, when immersed in water, and thus to pronounced solubility or dispersibility.

3.10. What is a van der Waal's liquid? Give few examples.

Ans: A polar liquids are often termed as van der Waal's liquids as their surface energy is constituted entirely of LW component. Most organic solvents are van der Waal's liquids.

3.11. What is Helmholtz instability?

Ans: The Kelvin–Helmholtz instability occurs when there is <u>velocity shear</u> in a single <u>continuous fluid</u>, or where there is a velocity difference across the interface between two fluids. An example is wind blowing over water: The instability manifests in waves on the water surface.

The theory predicts the onset of instability and transition to <u>turbulent flow</u> in <u>fluids</u> of different <u>densities</u> moving at various speeds. Helmholtz studied the <u>dynamics</u> of two fluids of different densities when a small disturbance, such as a wave, was introduced at the boundary connecting the fluids

For some short enough wavelengths, if surface tension is ignored, two fluids in parallel motion with different velocities and densities yield an interface that is unstable for all speeds. <u>Surface tension</u> stabilises the short wavelength instability however, and theory predicts stability until a velocity threshold is reached. The theory with surface tension included broadly predicts the onset of wave formation in the important case of wind over water.

3.12. Under what condition can a stable dispersion form?



Ans: Lets consider that two particles of material 1 is coming in contact in a liquid medium 3 (refer to adjoining figure). In order for a dispersion of material 1 to be stable in medium 3, the attachment of the two particles should be thermodynamically unflavored. This is possible when ΔG_{131} is positive, which therefore is the necessary condition for a stable dispersion.

Now we know that $\Delta G_{131} = -2 \Upsilon_{13}$ and

 $\Upsilon_{13} = \ \Upsilon_{13}{}^{AB} + \Upsilon_{13}{}^{LW}$

In order for ΔG_{131} to be positive, it becomes necessary for Υ_{13} to be negative.

Now, we also know that Υ_{13}^{LW} is always positive.

Therefore Υ_{13} can only be negative when Υ_{13}^{AB} is negative and higher in magnitude than Υ_{13}^{LW} , which is the necessary condition for a dispersion to be stable.

- 3.13. The surface tension of mercury at 0 C is 480.3 mJ/m² while the density is 13.595 g/cc. What must be the radius of the glass capillary tube for Hg to exhibit a fall in height of 10.0 cm? Use $\theta = 140^{\circ}$.
- Ans: The change in height due to capillary action is given by the following equation

 $h = 2 \gamma \cos(\theta) / (\rho g r)$

Given: $\gamma = 140 \text{ mJ/m}^2$

The required radius is:

 $r = 2 \cos(\theta) / (g h) = 2 0.4803 N/m \cos(140) / (13595 kg/m 9.81 m/s (-0.1m))$

 $r = 5.52 \ 10^{-5} m$

3.14. What is the pressure of a drop of liquid, when surface tension is 4 dynes and radius is 3mm?

Ans: $P_{drop} = 2 (4 \text{ dynes}) / .003 \text{ m} = 2666.6 \text{ dynes} / \text{ m}$

3.15. What is Maragoni Flow?

Ans: Any variation in surface tension along a layer of liquid results in a tangential (shear) forces, which are known as Marangoni forces. Such variation can arise from inhomogeneous material properties, or from temperature variations. Surface tension generally decreases with rising temperature which is one of the reasons we use hot water for washing clothes and utensils. Unless balanced by other forces shear surface forces cannot be sustained in a liquid at rest but will unavoidably set it into motion. Any flow resulting from Maragoni forces is known as Marangoni Flow.

3.16. How sap rises in plants?

Ans: Plants evaporate water through tiny pores on the surface of their leaves. This creates a hollow air-to-water surface with radii of curvature comparable to the radius r of the pore. Both centers of curvature lie outside the water, leading to a negative pressure excess in the water.

For a pore of one micron diameter, $2r = 1 \mu m$, the excess pressure inside the water will be $\Delta p = -2\gamma/r \approx 3$ atm. This pressure is capable of lifting sap through a height of

30 m, but in practice, the lifting height is considerably smaller because of resistance in the xylem conduits of the plant through which the sap moves. Taller plants and trees need correspondingly smaller pore sizes to generate sufficient negative pressures, even down to ≈ 100 atm!