Three phase contact lines.

Consider the case of two liquid drops in contact with each other

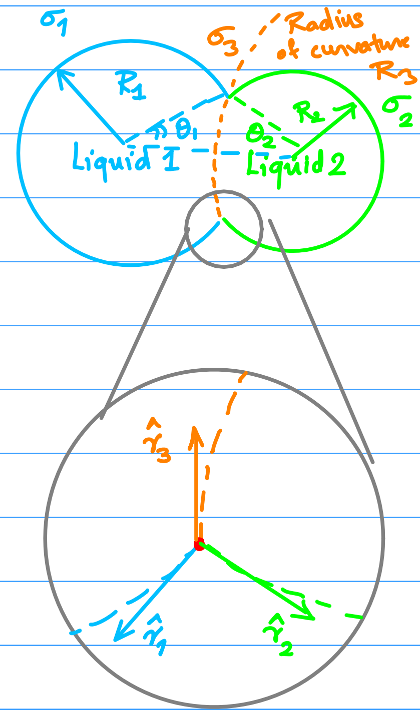


Figure 1. A 3-phase contact line.

Does this situation introduce any new concept? Given the volumes of the two drops and the three surface tensions, we desire to deduce the three radii of curvatures from physical principles.

Volume of drop 1 is given as V_1, but is related to (i) the radii of curvatures R_1 and R_3, and (ii) the angle where the spherical surface is truncated θ_1. $V_1 = V(R_1, R_3, \theta_1)$

Similarly, $V_2 = V(R_2, R_3, \theta_2)$

So far volume considerations give use 2 equations in 4 unknowns.

To attempt to find the additional equations, we use mechanics.

The pressure inside the drops may be obtained using Laplace pressure

$$P_1 = P_{atm} + \frac{2\sigma_1}{R_1}$$

$$P_2 = P_{atm} + \frac{2\sigma_2}{R_2}$$

These are two additional equations but they introduce 2 more unknowns P_1 and P_2. (assuming P_{atm} is known)

But these pressures can be related to each other through interface 3.

$$P_2 = P_1 + \frac{2\sigma_3}{R_3}.$$

That's an additional equation, but we are still one equation short.

This additional equation may be arrived at considering a force balance at the contact line (see zoomed view in **Figure 1**). The balance reads

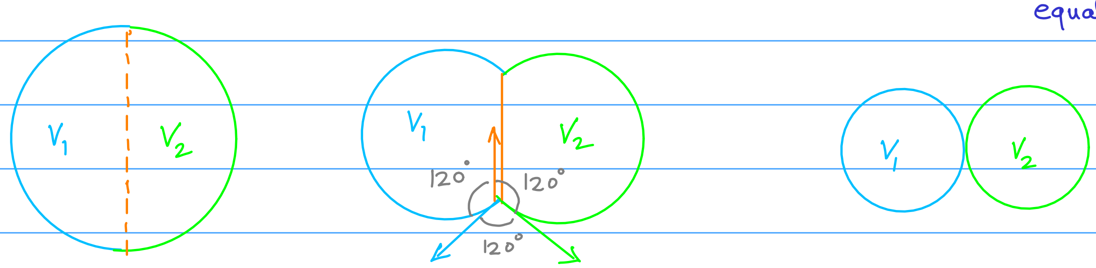
$$\sigma_1 \hat{r}_1 + \sigma_2 \hat{r}_2 + \sigma_3 \hat{r}_3 = \underline{0},$$

and thats the last equation.

Note that we cannot derive this equation using Laplace pressure or Marangoni stress.

Does a three drop situation introduce a fundamentally different force balance, not used in the two drop case?

Here are three simple limiting cases for the two drop problem (for simplicity consider equal volumes $V_1 = V_2$)



$\sigma_1 = \sigma_2$

$\sigma_3 << \sigma_1$ or σ_2 $\qquad$ $\sigma_3 = \sigma_1 = \sigma_2$ $\qquad$ $\sigma_3 \geqslant \sigma_1 + \sigma_2$

$\sigma_3 \neq 0$.

Thus, the two drops stay in contact if and only if $\sigma_3 < \sigma_1 + \sigma_2$. This conclusion can also be justified energetically by invoking that the surface tension also quantifies the surface energy, and when $\sigma_3 > \sigma_1 + \sigma_2$, the energy penalty of the two liquids touching (σ_3) is greater than the two liquids separately being in contact with air.

Contact line with a rigid solid phase.

A solid-liquid-gas (or a solid-liquid-liquid) contact line is shown in **Figure 2**. If such a configuration is possible, the balance of forces at the contact line may be written in terms of the equilibrium contact angle θ_{eq} as

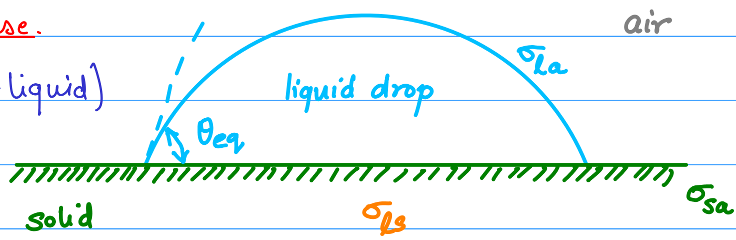


Figure 2: A solid-liquid-gas contact line.

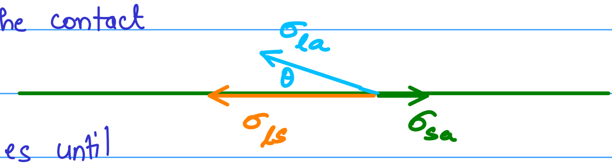
$\sigma_{sa} = \sigma_{ls} + \sigma_{la} \cos\theta_{eq}$. Another way to write this balance is $\cos\theta_{eq} = \dfrac{\sigma_{sa} - \sigma_{ls}}{\sigma_{la}}$

When does a configuration like the one shown in figure 2 exist?

The right hand side of this equation is defined as the wetting parameter. S

$S = \dfrac{\sigma_{sa} - \sigma_{ls}}{\sigma_{la}}$. Whenever this parameter is between $-1 < S < 1$, the configuration shown in **figure 2** exists.

When $S > 1$ (i.e $\sigma_{la} < \sigma_{sa} - \sigma_{ls}$), the liquid air surface energy is small and so is the surface tension. In such a case the contact line is pulled such that more liquid wets the solid. This process of wetting continues until the whole solid surface is wetted by a thin layer of the fluid. Any vapor of the fluid in air may also spontaneously condense on the surface, even if the conditions are such that bulk liquid spontaneously evaporates. A prewetted film of such liquids usually exists on such solid surfaces, and would be experimentally painstaking to remove. In the presence of such a liquid layer, the surface energy of the "coated surface" is equal to $\sigma_{la} + \sigma_{ls}$, as shown in figure 3. i.e. $\sigma_{sa,effective} = \sigma_{la} + \sigma_{ls}$.



Such a configuration therefore practically reduces to $S = 1$, and is known as completely wetting.

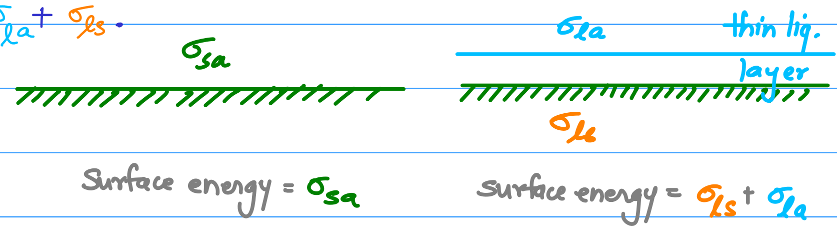


Figure 3: When $\sigma_{la} < \sigma_{sa} - \sigma_{ls}$ it is energetically beneficial to coat the surface with a (molecularly) thin layer of the liquid.

Similarly, if $S < -1$ (or $\sigma_{la} < \sigma_{sa} - \sigma_{ls}$), the liquid resists spreading completely. This situation is termed non-wetting.

When $-1 < S < 1$, The liquid partially wets the solid. The equilibrium contact angle in this case is (as we derived earlier)

$$\cos\theta_{eq} = \frac{\sigma_{sa} - \sigma_{ls}}{\sigma_{la}}, \quad \ldots$$

This equation is known as the Young – Dupré equation.

1805 1855.

We will soon make use of this angle.

Contact line with an elastic solid phase.

Just like the case of two liquid drops in contact, an additional force balance is required to complete the problem for liquids in contact with a deformable solid phase.

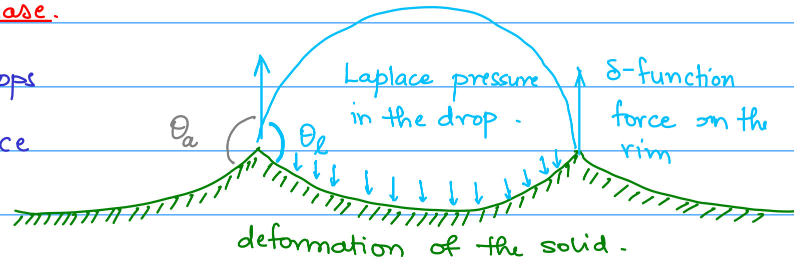


Figure 4: Contact line with an elastic solid

Along with a δ-function for force due to surface tension at the contact line, one also needs to impose a normal traction due to Laplace pressure in the drop, and a force balance at the contact line, similar to the zoomed view in Figure 1.

This is a topic of current investigation. See:
Style, Boltyanskiy, Che, Wettlaufer, Wilen, and Dufresne, Universal deformation of soft substrates near a contact line and the direct measurement of solid surface stresses, PRL, 110 (6), 066103, 2013.

Contact line motion:

Contact lines move in the direction of unbalanced tangential force. The speed with which they move is a topic of current research, but there is no doubt that they move in the direction of unbalanced tangential force.

Example: In Figure 5, since the unbalanced tangential force points to the right, the contact line moves in that direction.

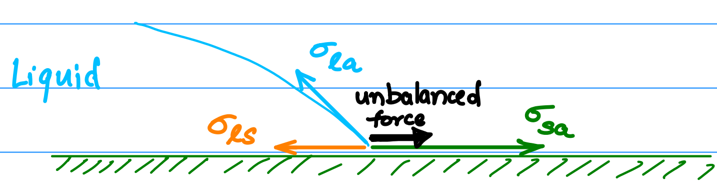


Figure 5: Contact lines move in the direction of unbalanced tangential force.

A runaway in the contact line motion is sometimes observed because the geometry of the solid surface is such that motion of the contact line is in a direction where the imbalance in tangential forces increases.

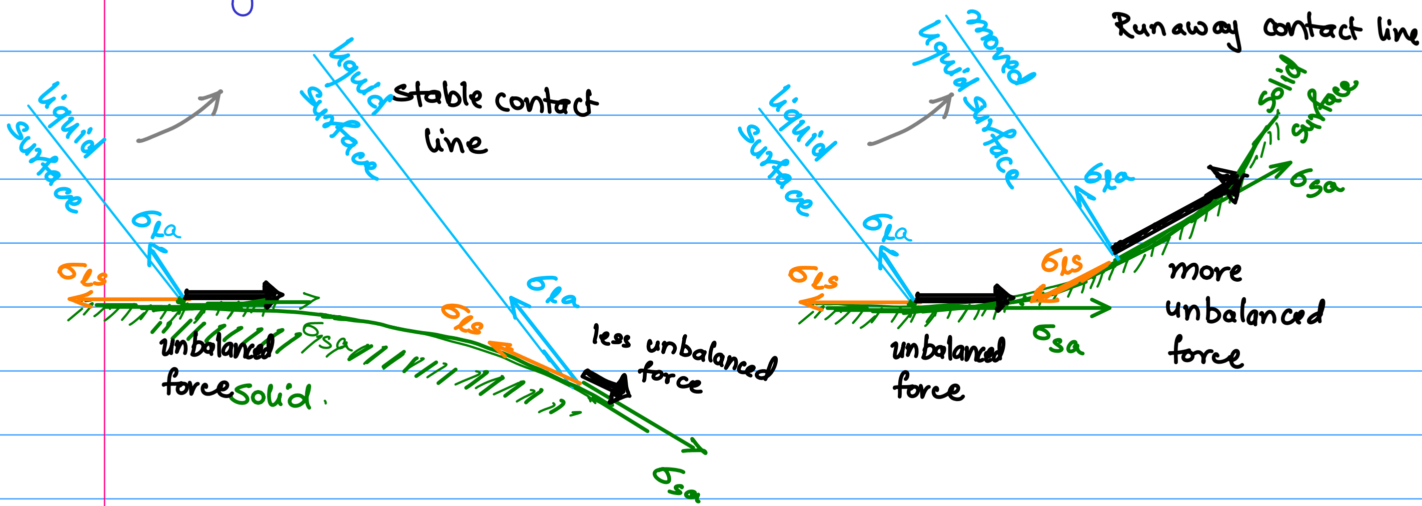
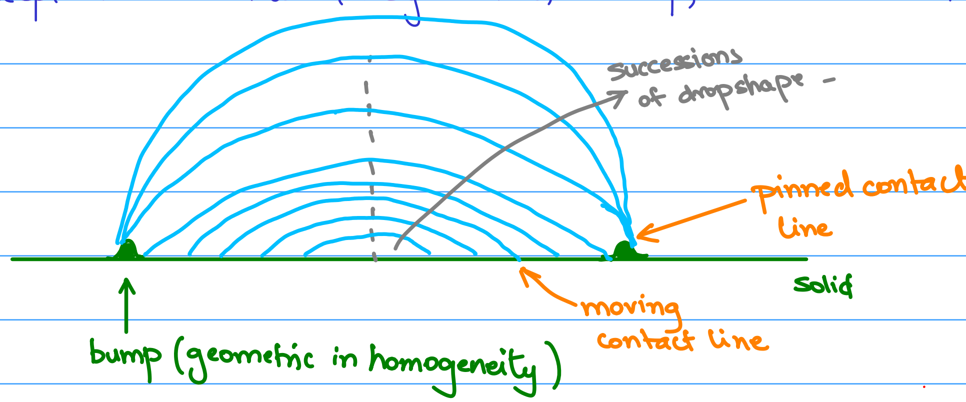


Figure 6: Change in the magnitude of unbalanced tangential force as the contact line moves determines whether the contact line runs away or not.

Contact line hysterisis, pinning, and stick-slip motion

Consider a drop being deposited on a rigid solid surface. The surface is smooth except for a small (axisymmetric) bump, as shown in figure 7.



Three concepts:

1. **Pinning** – As drop volume increases, the contact line first moves, but at the geometric inhomogeneity of the surface, it gets "pinned". The apparent contact angle (with the flat surface) increases, but the contact line does not appear to move.

   Microscopically forces are balanced, but macroscopically they APPEAR to be imbalanced.

2. **Stick-slip motion :** Once the drop volume increases beyond a critical, the contact line depins and jumps abruptly to a location further away from the geometric inhomogeniety. This motion is described as the slipping of the contact line (after the sticking that corresponded to the pinned contact line).

3. **Contact line hysterisis :** The location of the contact line and the shape of the drop are different as the drop volume is reduced (as compared to when it was increased). This behaviour is called contact line hysterisis.

These concepts are explained using a MATLAB demo.