3. Wetting

**Puddles.** What sets their size?
Knowing nothing of surface chemistry, one anticipates that Laplace pressure balances hydrostatic pressure
if $\sigma/H \geq \rho g H \Rightarrow H < \ell_c = \sqrt{\sigma/\rho g}$ = capillary length.

Note:
1. Drops with $R < \ell_c$ remain heavily spherical
2. Large drops spread to depth $H \sim \ell_c$ so that Laplace + hydrostatic pressures balance at the drop's edge. A volume $V$ will thus spread to a radius $R$ s.t. $\pi R^2 \ell_c = V$, from which $R = (V/\pi \ell_c)^{1/2}$.
3. This is the case for $H_2O$ on most surfaces, where a contact line exists.

Figure 3.1: Spreading of drops of increasing size.

Note: In general, surface chemistry can dominate and one need not have a contact line.

More generally, wetting occurs at fluid-solid contact. Two possibilities exist: partial wetting or total wetting, depending on the surface energies of the 3 interfaces ($\gamma_{LV}, \gamma_{SV}, \gamma_{SL}$).

Now, just as $\sigma = \gamma_{LV}$ is a surface energy per area or tensile force per length at a liquid-vapour surface, $\gamma_{SL}$ and $\gamma_{SV}$ are analogous quantities at solid-liquid and solid-vapour interfaces.

The degree of wetting determined by spreading parameters:

$$S = [E_{\text{substrate}]_{\text{dry}} - [E_{\text{substrate}]_{\text{wet}}} = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$$

where only $\gamma_{LV}$ can be easily measured.

**Total Wetting:** $S > 0$, $\theta_e = 0$ liquid spreads completely in order to minimize its surface energy. e.g. silicon on glass, water on clean glass.

Note: Silicon oil is more likely to spread than $H_2O$ since $\sigma_{w} \sim 70$ dyn/cm > $\sigma_{s.o.} \sim 20$ dyn/cm. Final result: a film of nanoscopic thickness resulting from competition between molecular and capillary forces.

**Partial wetting:** $S < 0$, $\theta_e > 0$. In absence of $g$, forms a spherical cap meeting solid at a contact angle $\theta_e$. A liquid is "wetting" on a particular solid when $\theta_e < \pi/2$, non-wetting or weakly wetting when $\theta_e > \pi/2$. For $H_2O$, a surface is hydrophilic if $\theta_e < \pi/2$, hydrophobic if $\theta_e > \pi/2$ and superhydrophobic if $\theta_e > 5\pi/6$.

Figure 3.2: The same water drop on hydrophobic and hydrophilic surfaces.

Note: if $g = 0$, drops always take the form of a spherical cap ⇒ flattening indicates the effects of gravity.