

for case C:

$$V = \frac{\pi R^3}{3} (1 - \cos \theta)^2 (2 + \cos \theta) + \pi R^2 h \sin^2 \theta - \frac{\pi}{3} m s^2 h \quad (8.10a)$$

$$A_L = 2\pi R^2 (1 - \cos \theta) \quad (8.10b)$$

$$A_{sL} = \pi R^2 \sin^2 \theta - m\pi s^2 + ms\sqrt{s^2 + h^2} \quad (8.10c)$$

where m is the number of asperities on the surface, h (m) is the profile height, l (m) is the distance between two consecutive peaks, s (m) is the half-base length of an asperity.

After eqn (8.4a-c) and eqn (8.10a-c):

$$\begin{aligned} \Delta G = & -\frac{\pi R^3}{3} \frac{\Delta\mu}{\Omega} (1 - \cos \theta)^2 (2 + \cos \theta) \\ & + 2\pi R^2 \gamma_L (1 - \cos \theta) - \pi R^2 (\gamma_s - \gamma_i) \sin^2 \theta \end{aligned} \quad (8.11)$$

To progress further, a mathematical correlation is required to link γ_L and the term $(\gamma_s - \gamma_i)$. When nucleation occurs on a non-porous (dense) surface, the Young equation can be used to express the mechanical equilibrium between interfaces:

$$(\gamma_s - \gamma_i) = \gamma_L \cos \theta \quad (8.12)$$

For a porous membrane, a modified form of the Young equation correlating the surface porosity to the measured and equilibrium contact angles can be adopted:²³

$$(\gamma_s - \gamma_i) = \gamma_L \left[\cos \theta + \frac{4\varepsilon(1 + \cos \theta)}{(1 - \varepsilon)(1 - \cos \theta)} \right] \quad (8.13)$$

For a rough membrane surface, the wetting behavior can be adequately described by the Wenzel equation:

$$(\gamma_s - \gamma_i) = \frac{1}{r_w} \gamma_L \cos \theta \quad (8.14)$$

where r_w is the Wenzel roughness factor ($r_w > 1$). For the case illustrated in Figure 8.3c, when assuming that asperities on the surface have a conical shape, the roughness factor r can be evaluated as:

$$r_w = \frac{(\pi l^2 - m\pi s^2) + m\pi s\sqrt{h^2 + s^2}}{\pi l^2} \quad (8.15)$$

In order to determine the Gibbs free energy barrier ΔG^* reached for a critical nucleus having radius R^* , the following maximization condition has to be applied: