

## Supporting Information

### i Derivation of the Generalized Young Laplace equation

We derive a generalized Young Laplace equation for a non-constant liquid-vapour surface energy  $\sigma(r) = \sigma_0 + \Delta\sigma(r)$  where  $\sigma_0$  is the equilibrium surface energy and  $\Delta\sigma(r)$  is small. The total Helmholtz free energy of a drop  $l$  on a surface  $s$  in equilibrium with the vapour  $v$  surrounding it is<sup>46</sup>

$$F = F_0 + 2\pi \int_0^{r_p} dr r \sigma \left( 1 + \left( \frac{\partial y}{\partial r} \right)^2 \right) + \pi r_p^2 (\sigma_{sl} - \sigma_{sv}) + 2\pi r_p E, \quad (11)$$

where  $y(r)$  is the liquid-vapour interface,  $\sigma_{sl}$  and  $\sigma_{sv}$  are the surface energies between the surface and the liquid and between the surface and the vapour,  $r_p$  is the radius of the drop at  $y(r)=0$ ,  $F_0$  is the shape-independent contribution to the free energy and  $E$  is the energy per unit length of the wetting perimeter. A minimization of the free energy subject to the constraint of constant volume  $V = 2\pi \int_0^{r_p} dr r y$  is on the expression

$$G = F - \chi V = \int_0^{r_p} dr f \left( r, y, \frac{\partial y}{\partial r} \right) + \psi(r_p) + F_0, \quad (12)$$

where  $f = 2\pi r \left( \sqrt{1 + (\partial y / \partial r)^2} \sigma - \chi y \right)$ ,  $\chi$  is the Lagrange multiplier, and

$\psi = \pi r_p^2 (\sigma_{sl} - \sigma_{sv}) + 2\pi r_p E$ . Assuming fixed contact radius ( $r_p$  is constant) the variation  $y(r) \Rightarrow y(r) + \delta y(r)$ , where  $\delta y(r)$  is small, results with variation in  $G$  in the form

$$\delta G = \int_0^{r_p} dr \left( \frac{\partial f}{\partial y} - \frac{d}{dr} \frac{\partial f}{\partial (\partial y / \partial r)} \right) \delta y. \quad (13)$$

For  $\delta G = 0$ , assuming arbitrary  $\delta y$ , we obtain the Young Laplace equation

$$\frac{1}{r} \frac{\partial}{\partial r} \left( \frac{r (\partial y / \partial r)}{\sqrt{1 + (\partial y / \partial r)^2}} \right) + \frac{1}{\sigma} \frac{\partial \sigma}{\partial r} \frac{\partial y / \partial r}{\sqrt{1 + (\partial y / \partial r)^2}} + \frac{\chi}{\sigma} = 0, \quad (14)$$

subject to the contact angle between the liquid-vapour and the liquid-solid surfaces. As the middle term is  $O((\partial \sigma / \partial r) / \sigma)$  with respect to the first while the third satisfies the equality, eq 14 can be written as:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( \frac{r(\partial y / \partial r)}{\sqrt{1 + (\partial y / \partial r)^2}} \right) + O \left( \frac{1}{\sigma} \frac{\partial \sigma}{\partial r} \right) + \frac{\chi}{\sigma_0} = 0 \text{ with } \chi = 2\sigma_0 / R, \quad (15)$$

which quantify the error in the local curvature and in the Laplace pressure in eq 1 due to deviations of the surface tension from equilibrium.

## ii Asymptotic boundary condition for the surface pressure

As the diffusion and convection characteristic time scales at the extent of the bubble are much slower than the experiments time scale, the concentration of impurities should not vary from its equilibrium value as first approximation. Therefore, in the limit of  $r \rightarrow \infty$ , which is identified with the length scale of the radius of the drop  $O(R_b)$  from the interacting apex,  $\pi_s \rightarrow \pi_{s0}$ . Assuming negligible deformations  $h = h_{init} + r^2 / 2R_b$  and integrating from the origin of the film thinning equation (eq 8a),

$$\frac{\partial \pi_s}{\partial r} = \mu \frac{\partial h}{\partial r} \frac{r}{h^2} - \frac{2}{3} h \frac{\partial p}{\partial r}. \quad (16)$$

In the limit of large  $r$ <sup>17</sup> the hydrodynamic pressure  $p \rightarrow 1/r^4$  and the thickness of the film  $h \rightarrow r^2$ . The two terms to the right side of eq 15 decay as  $1/r^2$  and  $\pi_s$  can be represented as  $c'/r^2$ , where  $c'$  is a constant. Integration from infinity yields the asymptotic boundary condition

$$r(\partial \pi_s / \partial r) + 2(\pi_s - \pi_{s0}) = 0 \text{ at } r = r_{\max} \quad (17)$$

that relates the surface pressure at the scale of the drop to its value at  $r_{\max}$ . (The factor 2 in this equation has been omitted from reference 33 due to a typographical error.) Note that  $r_{\max}$  is large compare to the radial value around the interacting drop apex, but small compare to the radius of curvature of the bubble,  $r^* \ll r_{\max} \ll R_b$ .