Compound sessile drops – ESI

Michael J. Neeson,ab Rico F. Tabor,bc∗ Franz Grieser,bd Raymond R. Dagastine be and Derek Y. C. Chan abf

1 Mathematical details

The solutions of the Young–Laplace equation for the interfaces of axisymmetric compound sessile drops are outlined in this section.

1.1 Sessile drop with a lens

![Diagram of a sessile drop with a lens]

Fig. 1 A schematic representation of the three-phase contact region of a lens on a sessile drop comprising 3 mutually immiscible fluids with interfacial tensions γ12, γ13 and γ23. Inset: A spherical cap of volume Vcap with base radius a and subtends an angle ψ.

† Electronic Supplementary Information (ESI) available: Ancillary results and videos of evaporating drops on different substrates. See DOI: 10.1039/b000000x/

The first integral of the Young–Laplace equation, eqn. (3) in the main text, that describes an axisymmetric interface is

\[ r \sin \phi = \frac{r^2}{R} + C. \] (1)

For the 13- and 23-interface, the boundary conditions in eqns (4a) and (4b) imply that the constant of integration C = 0. Therefore the equation for these interfaces are (see Fig. 1)

\[ r_{23}(\phi_{23}) = R_{23} \sin \phi_{23}, \quad r_{13}(\phi_{13}) = R_{13} \sin \phi_{13}. \] (2)

These are equations for spherical caps of radii R23 and R13.

For the 12-interface the condition that it meets the substrate at \( r_{12} = a_{12} \) with contact angle \( \phi_{12} = \theta_{12} \) means that the first integral has the form

\[ r_{12} \sin \phi_{12} = \frac{r^2_{12}}{R_{12}} - \left[ \frac{a_{12}^2}{R_{12}} - a_{12} \sin \theta_{12} \right]. \] (3)

The force balance condition in eqn (8) of the main text implies that the term

\[ G \equiv \left[ \frac{a_{12}^2}{R_{12}} - a_{12} \sin \theta_{12} \right] = 0. \] (4)

Therefore the 12-interface is also a spherical cap, of radius \( R_{12} \)

\[ r_{12}(\phi_{12}) = R_{12} \sin \phi_{12}. \] (5)

1.2 Sessile drop with a collar

The 12- and 23-interface meets the substrate at \( r = a_{12} \) or \( a_{23} \) with contact angle \( \phi = \theta_{12} \) or \( \theta_{23} \) (see Fig. 2). The first integral of the Young–Laplace equation for each of these two interface can be written as

\[ r \sin \phi = \frac{r^2}{R} - \frac{a^2}{R} - a \sin \theta \equiv \frac{r^2}{R} - G \] (6)

where we have suppressed the subscripts 12 and 23. This can be solved for \( r(\phi) \)

\[ r(\phi) = \frac{R}{2} \left( \sin \phi \pm \sqrt{\sin^2 \phi + \frac{4G}{R}} \right) \] (7)

where the choice of sign is taken to ensure \( r(\phi = \theta) = a \).
The height, $z$ of the interface above the substrate can be found by integration

$$z(\phi) = \int_{\theta}^{\phi} d\phi \frac{dz}{d\phi}$$

$$= \int_{\theta}^{\phi} \tan \phi \left\{ \frac{R}{2} \left( \cos \phi \pm \frac{\sin \phi \cos \phi}{\sin^2 \phi + 4G/R} \right) \right\} d\phi$$

$$= \frac{R}{2} \left[ -\cos \phi \pm \frac{1}{\sqrt{R/(4G)}} \left\{ E \left( \frac{\phi - R}{4G} \right) - F \left( \frac{\phi - R}{4G} \right) \right\} \right]$$

where $F(\phi|m)$ and $E(\phi|m)$ denote incomplete elliptic integrals of the first and second kind, defined by

$$F(\phi|m) \equiv \int_{0}^{\phi} \frac{1}{\sqrt{1 - m \sin^2 \theta}} d\theta$$

$$E(\phi|m) \equiv \int_{0}^{\phi} \sqrt{1 - m \sin^2 \theta} d\theta.$$

In general one must consider all possible choices of sign for $R$ and $G$, however for the 12- and 23-interfaces considered here, $R$ and $G$ have the same sign and so we restrict ourselves to the case $G/R > 0$. The above expressions for $r$ and $z$ give the position of the 12- and 23-interfaces as functions of the tangent angles $\phi_{12}$ and $\phi_{23}$ (see Fig. 2)

Although we have established the mathematical relationship between all variables, the method for determining the values of these parameters is very important. We therefore outline the algorithm used to find the given parameters.

To fit these solutions to experimental images of compound sessile drops with a collar, the software package ImageJ was used to first binarise the images, and then extract the profile as a list of coordinates. We then minimised the squared residuals as follows:

1. locate the 3-phase contact point, using a local minimum of the profile width, and split the image horizontally
2. use least squared fit to the top half to a sphere to obtain the radius $R_{13}$, and the horizontal position of the centre of the image
3. calculate the angle $\beta$ from the height of the 3-phase contact, and the fitted radius, and then determined the radial position, $a$ of the 3-phase contact line and the angle $\omega$
4. pick a value for Laplace radius $R_{12}$
5. ensuring $r_{12}(\pi - \omega) = a$ sets the value of $G_{12}$
6. construct the 12-interface using $r_{12}(\phi)$ and $z_{12}(\phi)$, then compare this to experimental data using a ‘distance-squared’ objective function
7. adjust $R_{12}$ and repeat process until a minimum is obtained
8. vary $\beta$ within experimental error and repeat steps 5-8.

2 Supplementary videos

We include three movies of the evaporation of a water collar around a mercury drop:

1. Movie 1 - on a hydrophilic glass substrate
2. Movie 2 - on a semi-hydrophobic glass substrate
3. Movie 3 - on a hydrophobic glass substrate.