Evaporation of a capillary bridge between a particle and a surface – ESI

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1 Particle position

In this section we calculate the centre of mass of a particle-spherical interface system, which then determines the force acting on the particle and hence the position of the particle on the spherical interface.

We consider a spherical drop with a particle attached to its interface as depicted in Fig. 1. We begin by considering a

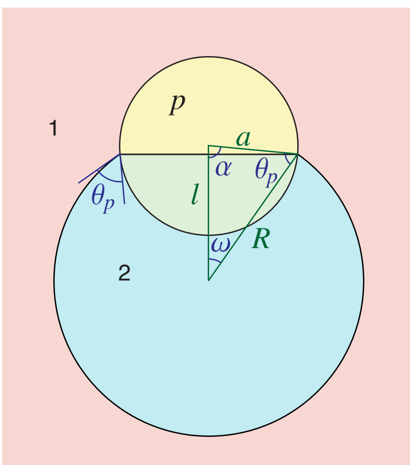

Fig. 1 A spherical particle p attached to the interface of a spherical drop of fluid 2, surrounded by outer phase 1.

particle which is sitting at the zenith of the drop. Taking the axes origin to be the centre of the drop, we denote the centre of mass of the system d, measured in the positive z direction. By symmetry about the z-axis, the centre of mass will be $\mathbf{c} = (0,0,d)$, where

$$\mathbf{c} = \iiint \boldsymbol{x}\,\rho(\boldsymbol{x})\,dV \Big/ \iiint \rho(\boldsymbol{x})\,dV$$
$$= \frac{\iiint_{particle} \boldsymbol{x}\Delta\rho_{1p}\,dV + \iiint_{fluid\,2} \boldsymbol{x}\Delta\rho_{12}\,dV}{\Delta\rho_{1p}\iiint_{particle} dV + \Delta\rho_{12}\iiint_{fluid\,2} dV} \tag{1}$$

where $\Delta\rho_{ij} \equiv \rho_j - \rho_i$ is the difference between the two densities for phase i and j. The quantity d can be written as the weighted average of the centre of mass for both the drop d_2 and the particle d_p

$$d = \frac{\Delta\rho_{1p}V_p d_p + \Delta\rho_{12}V_2 d_2}{\Delta\rho_{1p}V_p + \Delta\rho_{12}V_2} \tag{2}$$

where V_2 and V_p are the volumes of the drop and the particle, respectively. In the preceding expression the quantity V_2 is the volume of the supporting drop 2. To simplify the expression for d_2 we add and subtract a volume of fluid corresponding to the fluid removed by the presence of the particle (denoted by the $e \equiv e_1 + e_2$), which is depicted in Fig. 2. This allows d to be written

$$d = \frac{\Delta\rho_{1p}V_p d_p + \Delta\rho_{12}(V_{2+e}d_{2+e} - V_e d_e)}{\Delta\rho_{1p}V_p + \Delta\rho_{12}V_2}. \tag{3}$$

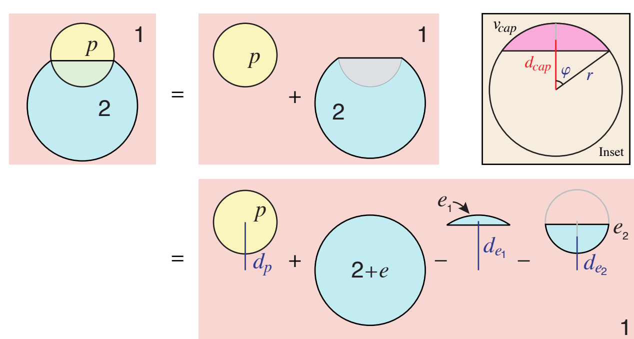

Fig. 2 A cartoon depicting the initial particle drop system split into a series of different domains to facilitate the calculation of the centre of mass of the system. Inset: A spherical cap with volume v_{cap} and centre of mass d_{cap} formed by taking a portion of a sphere of radius r, with subtended angle φ.

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

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The centre of mass of the newly formed body $2+e$ is simply the centre of mass of a sphere centred at the origin, which is zero.

All the quantities in the preceding expression for the centre of mass can be expressed in terms of the volume v_{cap} and centre of mass d_{cap} of a spherical cap, which can be written

$$v_{cap}(r,\varphi) = \frac{\pi r^3}{3}(2-3\cos\varphi+\cos^3\varphi) \tag{4a}$$

$$d_{cap}(r,\varphi) = \frac{3r}{4}\frac{(1+\cos\varphi)^2}{2+\cos\varphi} \tag{4b}$$

where r is the radius of the sphere and φ is the subtended angle, as illustrated in Fig. 2.

By applying the law of cosines to the angle formed between the centre of the particle, the centre of the supporting spherical interface, and the three phase contact allows the distance between the two particles l, and the filling angle α to be expressed in terms of the drop radius

$$l^2 = a^2 + R^2 - 2aR\cos\theta_p \tag{5a}$$

$$R_2 = a^2 + l^2 - 2al\cos\alpha. \tag{5b}$$

Finally, the centre of mass of the system can be expressed as

$$d = \frac{\Delta\rho_{1p}V_p d_p - \Delta\rho_{12}(V_{e_1}d_{e_1} + V_{e_2}d_{e_2})}{\Delta\rho_{1p}V_p + \Delta\rho_{12}V_2} \tag{6}$$

where the expressions for volume and centre of mass of each of the regions is given by

$$V_p = \frac{4\pi}{3}a^3 = v_{cap}(a,\pi) \qquad d_p = l \tag{7a}$$

$$V_{e_1} = v_{cap}(R,\omega) \qquad d_{e_1} = d_{cap}(R,\omega) \tag{7b}$$

$$V_{e_2} = v_{cap}(a,\alpha) \qquad d_{e_2} = d_p - d_{cap}(a,\alpha) \tag{7c}$$

$$V_2 = \frac{4\pi}{3}R^3 - (V_{e_1}+V_{e_2}) \qquad d_2 = 0, \tag{7d}$$

together with the introduction of the angle $\omega = \pi - (\alpha+\theta_p)$. Substituting these expressions into eqn (6), and noting that

$$d_{cap}(r,\varphi)\,v_{cap}(r,\varphi) = \frac{\pi}{4}r^4\sin^4\varphi \tag{8}$$

then gives

$$d = l\,\frac{\Delta\rho_{1p}v_{cap}(a,\pi) - \Delta\rho_{12}v_{cap}(a,\alpha)}{\Delta\rho_{1p}V_p + \Delta\rho_{12}V_2} \tag{9}$$

where we have used the equality of $R\sin\omega = a\sin\alpha$ by applying the Law of Sines to the triangle formed in Fig. 1.

This configuration can be rationalised as a particle rotating with its centre distance l from the centre of the spherical drop. The centre of mass of this system acts at some distance d from the centre of the drop, with gravity acting on a volume of effective mass $m_{eff} = \Delta\rho_{1p}V_p + \Delta\rho_{12}V_2$, with a force $m_{eff}g$. This means that the gravitational force acting on particle will be either upwards or downwards, depending on the sign of the expression $S(\alpha)$, which is

$$S(\alpha) = \Delta\rho_{12}\bar{v}_{cap}(\alpha) - \Delta\rho_{1p}\bar{v}_{cap}(\pi), \tag{10}$$

where $\bar{v}_{cap}(\varphi)$ is the scaled cap volume $\bar{v}_{cap}(\varphi) \equiv v_{cap}(r,\varphi)/r^3$, and we have used the property that $l>0$.

This result can be applied to the particle-drop-substrate configuration as follows. If a sessile drop is formed on the substrate, positive S will result in a gravitational force acting upwards on the particle, ultimately positioning the particle axisymmetrically at the drop apex. Conversely, for negative S the particle will experience a force downward, positioning it at the substrate. The opposite result holds for a pendant drop.

Interestingly, the above expression is dependant on the filling angle α, which in turns depends on the drop radius and hence the drop volume. It is therefore possible for a particle initially at the apex of the supporting drop to reposition itself at the substrate partway through the evaporation of the supporting drop.

2 Supplementary videos

We include four movies of the evaporation of a water capillary bridge formed between a particle and a substrate:

1. Movie 1 – a silica particle below a PTFE substrate
2. Movie 2 – a silica particle below a gold substrate
3. Movie 3 – a polystyrene particle above a polystyrene substrate
4. Movie 4 – a silica particle above a PMMA substrate.