The multitude of aesthetic shapes that liquid drops adopt in various situations has always been fascinating to human beings; the formulations by Young and Laplace attracted physicists and mathematicians alike to solve such shapes. Pendant drops hanging from a flat surface are seen very frequently, e.g. after rains, in limestone caves, and in situations of condensation. These drops are held in a state of static equilibrium under the action of gravity and surface forces. Many shapes of pendant drops are possible for a given volume, and our study reveals one such class of shapes. To the best of our knowledge, studies of pendant drops hanging from solid surfaces, which obtain shapes through an energy minimization procedure, all hold a fixed area of contact with the solid. Correct drop shapes are then obtained by additionally imposing Young’s relation at the solid surface. In contrast, we allow the contact area to vary during minimization of energy. DROP shapes obeying Young’s relation emerge naturally in our procedure. More interestingly, we obtain a new class of static minimum-energy drop shapes. These do not satisfy Young’s relation, but have zero net force everywhere. They are stable to symmetric perturbations satisfying force balance.

We study both two-dimensional and axisymmetric drops. Consider a liquid drop suspended downwards from a horizontal solid surface, subjected to gravity and surface forces. The shape of the liquid-gas interface is described by $x(z)$ or $r(z)$, where $x$ for a two-dimensional drop is the horizontal distance of the liquid-gas interface from the $z$-axis, and $r$ is the corresponding radial distance for an axisymmetric drop. We write

$$E_0 = \int_0^h \left[ \gamma \sqrt{1 + x'^2} - \rho g x (h - z) \right] dz + (\gamma_{sl} - \gamma_{sq}) \lambda$$

(1)

where the total energy for a two-dimensional drop is $2E_0$. The solid plate is taken to be the base for potential energy. The drop is characterized by its total height $h$ and the solid-liquid interface half-length $\lambda$. The functional $E_0$ must be extremised subject to the constraint of constant volume $V$. We consider a perturbed shape $\hat{x} = x + \epsilon\eta(z)$ where $\epsilon$ is a small parameter. Correspondingly the end point moves to $[\hat{\lambda} = \lambda + \epsilon\Lambda, \hat{h} = h + \epsilon H]$. Unlike fixed boundary-value problems in variational calculus, the solutions to free end-point problems automatically yield the required additional boundary conditions, which are implicit in the problem formulation, so our approach holds appeal in that (i) a class of solutions of extremum energy that we obtain automatically subtend Young’s contact angle $\theta_e$, (ii) we also obtain shapes which subtend a different angle at the contact line, which satisfy force balance nevertheless, and are of minimum energy.

Thus, we get Euler-Lagrange equation, $z - \chi = \frac{d}{dz} \left( \frac{x_s}{\sqrt{1 + x'^2}} \right)$, offering a drop shape for every $r_0$, so we reduce the solution space to a one dimensional space in the Lagrange multiplier, all of which ensure force balance everywhere. Shapes of minimum or maximum energy may then be picked from these. In addition to the force balance, we get the boundary condition to be

$$\frac{\epsilon \Lambda}{\epsilon H} \left( \cos \theta_s + \frac{\gamma_{sl} - \gamma_{sq}}{\gamma} \right) = 0.$$  

(2)

If we set the quantity within the brackets to zero, we see that $\theta_s$ is equal to the equilibrium contact angle $\theta_e$, to the automatic satisfaction of Young’s equation of local surface tension balance. However, equation (2) can also be satisfied when $\epsilon \Lambda/\epsilon H = 0$. This will happen when the perturbed solution contains no terms of $O(\epsilon)$ in $\lambda$, i.e., when $\lambda$ is at an extremum. By construction such solutions display an extremum in energy and satisfy force balance everywhere.

The shape for each $r_0$ is obtained by numerical integration, and then energy is obtained as a function of the shape factor. While shapes satisfying Young’s equation, which we refer to as Y solutions, are long known, we show that the second condition of (2) leads to a new solution branch of static drops. Moving in $r_0$ space, one reaches the new branch when $d\lambda/dr_0 = 0$. We find numerically that the second variation of $\lambda$ for these solutions is always positive, so we call them minimum contact-area or MCA solutions. The MCA is thus the result of a macroscopic energy minimization, and would presumably require a hysteretic (non-ideal) surface to manifest itself, so that forces at microscopic length scales may dominate near the surface. The branches exchange
FIG. 1: Volume of extremum energy shapes as a function of height. Curves I to V correspond to Y solutions. The MCA solutions lie along $FECD$. Minimum energy solutions are shown by the symbols, so $B$ and $E$ are bifurcation points. Drop shapes shown in the insets correspond to ‘a’ with $V = 1.25$, ‘b’ with the same volume, and ‘c’ on MCA with $V = 2.0$. Points below $AFGH$, including the dashed lines, have unphysical drop shapes.

FIG. 2: Exchange of stabilities at the transcritical bifurcation point $E$ for $\theta_e = 70^\circ$. Stable regions are shown by the symbols. Curves I and II show the total energy as a function of drop height for $V = 1.1$ and 1.55 respectively. The scales are different for the two curves. The MCA solution is unstable in curve I, while the Y solutions are stable. On curve II, the MCA shape is stable while the second Y solution becomes unstable. The inset shows that the contact area $\lambda$ is at a minimum for the MCA solution.

stabilities at a certain volume through a transcritical bifurcation, so the MCA solutions constitute stable minimum-energy drop shapes at higher volumes (Figures 1 and 2). These conclusions have been extended to axisymmetric pendant drops and found the existence of infinitely many Y and MCA branches.

We show analytically that two-dimensional drops can never be taller than 3.42 times the capillary length. We show numerically that the height of an axisymmetric drop has no limit, but the volume is always finite. We note that our procedure only ensures linear stability of the drop to axisymmetric perturbations which obey the same force balance. Since the energy well MCA branch is shallower compared to Y branch, nonlinearities can become important and presence of extraneous forces, even if small, could play spoilsport, especially at the extremely narrow neck regions. Also, MCA solutions are the result of macroscopic energy minimization where the only relevant length scale is the capillary length. At smaller length scales, intermolecular interactions manifest themselves in various ways at the contact line and a generalised Young’s equation may be adopted. The MCA would be consistent with these as well.