

# Simple Model of Compressive Force Curve

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## 1 Preface

I wanted to preface this document by saying that while I believe everything it contains is *correct*, I would be surprised if much, if anything, is *novel*. My goal is simply to present a simple model, developed from first principles, with the aim of fitting (and hopefully aiding the interpretation of) experimental data.

## 2 Thermodynamic Analysis

Consider a fine droplet of an incompressible fluid surrounded by a second incompressible fluid in which it is immiscible (see Figure 1). Suppose the fine droplet is compressed between two flat plates. We are interested in calculating the force curve of the compression (i.e. calculating the compressive force as a function of the distance of compression.)

In principle this is a complicated problem, particularly if surfactants are present, or if the droplet has capsule-like properties. In what follows, we will conduct an idealised analysis of the system. We assume the compression is reversible, so thermodynamic arguments may be applied. We assume that the overall system comprising the droplet, the surrounding fluid, and the surface which separates them has uniform temperature,  $T$ , and constant total volume. Finally, we assume that change in the interfacial area of the droplet and surrounding liquid,  $dA_{d-l}$  increases the interface's free energy by  $\gamma_{d-l}dA_{d-l}$ , where  $\gamma_{d-l}$  is an appropriate interfacial energy, which is assumed to be constant. Changes in the droplet-solid interfacial area,  $A_{d-s}$ , and the solid-surrounding liquid interfacial area,  $A_{s-l}$ , will lead to similar changes in their respective free energies. Any mechanical stiffness or elasticity in the droplet (or capsule) shell is ignored.

Suppose the flat plates compressing the droplet are separated by some distance  $l \leq 2R$ , where  $R$  is the radius of the uncompressed spherical droplet, and suppose this distance is reduced by some infinitesimal amount  $-dl$ . Then as the entire system is at constant volume and temperature, the work required to achieve this compression reversibly will be equal to the increase in the *Helmholtz Free Energy*<sup>1</sup> of the system, which is given by:

$$d\mathcal{F}_{\text{sys}} = d\mathcal{F}_{\text{drop}} + d\mathcal{F}_{\text{surr}} + d\mathcal{F}_{\text{surf}} \quad (1)$$

From the fundamental thermodynamic relation and the expression for the free energies of the surfaces:

$$d\mathcal{F}_{\text{sys}} = -S_{\text{drop}}dT - p_{\text{drop}}dV_{\text{drop}} - S_{\text{surr}}dT - p_{\text{surr}}dV_{\text{surr}} + \sum_i \gamma_i dA_i \quad (2)$$

where the final summation is over all surfaces in the system (specifically,  $A_{d-l}$ ,  $A_{d-s}$  and  $A_{s-l}$ .)

As the entire system is isothermal and the two fluids are incompressible,

$$dT = dV_{\text{drop}} = dV_{\text{surr}} = 0, \quad (3)$$

and so the change in the Helmholtz Free Energy is given by:

$$d\mathcal{F}_{\text{sys}} = \sum_i \gamma_i dA_i \quad (4)$$

As the change in free energy is induced by the reversible compression of the droplet at constant temperature and constant *overall* system volume,  $d\mathcal{F}_{\text{sys}}$  is equal to the reversible work of compression, which may be related to the force of compression,  $F$ , and the distance of compression  $-dl$ , by:

$$d\mathcal{F}_{\text{sys}} = -Fdl = \sum_i \gamma_i dA_i, \quad (5)$$

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<sup>1</sup>There are two advantages to using the Helmholtz Free Energy rather than the Gibbs Free Energy. First, the value of the Helmholtz Free Energy in a bulk fluid is independent of the pressure at constant volume and temperature, because  $d\mathcal{F} = -SdT - pdV$  (see Denbigh's *Principles of Chemical Equilibrium*). This is in contrast to the Gibbs Free Energy, which *is* affected by pressure changes even under isochoric, isothermal conditions, as  $d\mathcal{G} = -SdT + Vdp$ . If the Gibbs Free Energy were used, the change in the internal droplet's Laplace pressure caused by the deformation of the interface would need to be accounted for in calculating the change in  $\mathcal{G}$  for the fluid inside the droplet, but this calculation is not required when using the Helmholtz Free Energy. Second, the Helmholtz Free Energy is a work-potential for a composite isothermal system with total constant volume (as occurs here, as all fluids are incompressible). Hence,  $d\mathcal{F}_{\text{sys}} = dW$  in a reversible process, and from this it also follows that the Helmholtz Free Energy is minimised (or at least stationary) when the system is at equilibrium. The Helmholtz Free Energy could not easily be used if one or both of the fluids were compressible.

and so

$$F = - \sum_i \gamma_i \frac{dA_i}{dl}. \quad (6)$$

Hence, the force curve,  $F(l)$ , may be calculated given knowledge of (a) the interfacial energies,  $\gamma$ , and (b) the way in which the interfacial areas,  $A_i$ , change with the separation between the compressive plates,  $l$ .

### 3 Shape of Deformed Droplet

In earlier calculations, the shape of the compressed droplet was assumed to be a solid of revolution with semi-circular bulges rotated around a central vertical axis. While this may be a reasonable first approximation, there is no reason to expect that the free surfaces of the compressed droplet will conform to this particular shape.

Instead, the shape of the free surfaces may be solved via a Calculus of Variations problem. As the compression is reversible, isothermal and isochoric the droplet's shape at each moment will be such as to minimise the overall Helmholtz Free Energy of the system, given the separation of the flat plates,  $l$ , and the constant-volume constraint. As shown in Eq. (4), the variation in the Helmholtz Free Energy depends the variation of area of each of the three kinds of interfaces in the system, and a necessary condition for a minimum of the Helmholtz Free Energy is that:

$$d\mathcal{F}_{\text{sys}} = 0 = \gamma_{d-l}dA_{d-l} + \gamma_{d-s}dA_{d-s} + \gamma_{s-l}dA_{s-l} \quad (7)$$

If it is assumed that each of the  $\gamma_i$  are constant, this is equivalent to the statement that the following functional is stationary at equilibrium:

$$\mathcal{J} = \gamma_{d-l}A_{d-l} + \gamma_{d-s}A_{d-s} + \gamma_{s-l}A_{s-l} \quad (8)$$

where  $\mathcal{J}$  is a functional which depends on the shape of the compressed droplet.

To begin the analysis, consider the free interface between the droplet and the surrounding liquid. It is assumed that this is a surface of revolution, as suggested by the symmetry of the system, and so specification of the function  $y(x)$  in Figure 1 completely specifies the geometry of the deformed droplet. One symmetrical boundary condition for  $y(x)$  may be specified immediately:

$$y'(x = 0) = 0. \quad (9)$$

It is not immediately obvious whether a second boundary condition may be specified at  $x = l/2 = \delta$ . The value of  $y(x = \delta)$  will determine the area of the

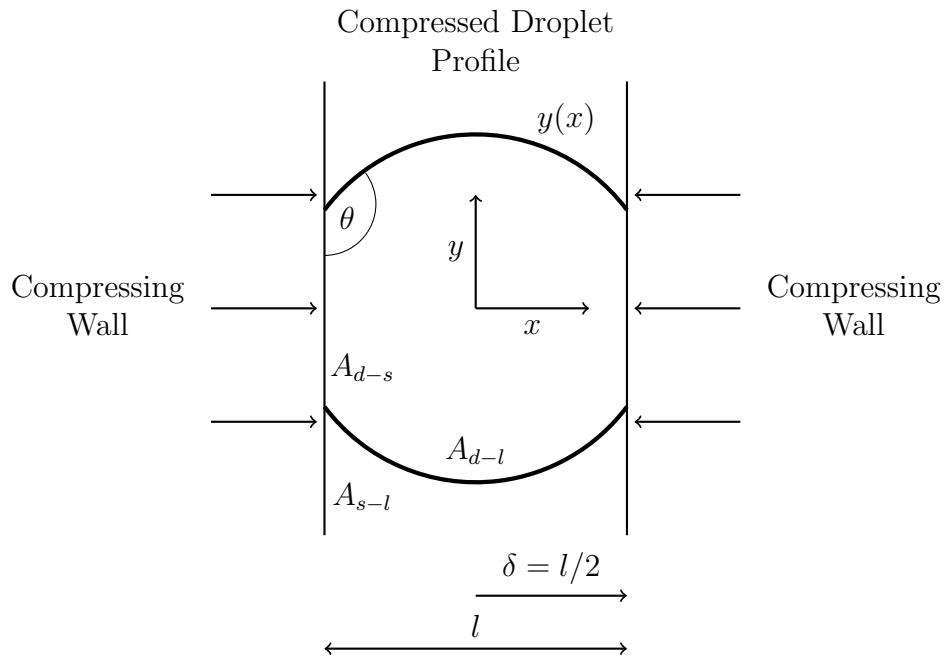


Figure 1: Profile of droplet being compressed between two parallel plates. The droplet is assumed to be a solid of revolution, defined by rotating the function  $y(x)$  around the  $x$  axis.

droplet-solid interface and surrounding liquid-solid interface, and it would be possible to leave this value unspecified and treat it as a variable within the larger problem of minimising the Helmholtz Free Energy. However, it is possible to show (c.f. Roura and Fort, J. Col. Int. Sci. 272(2) (2004): 420-429) that for a system at thermodynamic equilibrium, the *contact angle* at the interface may be related to the various surface tensions via Young's Equation:

$$\gamma_{d-l} \cos \theta + \gamma_{d-s} = \gamma_{s-l} \quad (10)$$

The contact angle then provides a second boundary condition for  $y(x)$ :

$$y'(x = \delta) = \cot \theta. \quad (11)$$

Once boundary conditions for  $y(x)$  and the constant-volume constraint have been specified, determining the shape of the liquid-liquid surface may be treated as an independent problem, as the configuration of the compressed droplet which *globally* minimises the Helmholtz Free Energy (accounting for all surfaces in the system) will necessarily (for constant  $\gamma_{d-l}$ ) lead to the liquid-liquid surface in particular being a minimal surface (i.e.  $y(x)$  will be an extremum of a certain integral, and will satisfy certain Euler-Lagrange equations.) Only one minimal surface exists which is consistent with the two boundary conditions and the constant volume constraint, and in this way  $y(x)$  (and in turn the shape of the compressed droplet) may be uniquely determined. These statements will be demonstrated mathematically below.

### 3.1 Mathematical Formulation

In terms of the function  $y(x)$  defined above, the volume of compressed capsule is given by:

$$V = \frac{4}{3}\pi R^3 = 2 \int_0^\delta \pi y(x)^2 dx = 2\pi \int_0^\delta y(x)^2 dx \quad (12)$$

The liquid-liquid surface area of the compressed capsule is:

$$A_{d-l} = 2 \int_0^\delta 2\pi y(x) \sqrt{1 + y'(x)^2} dx = 4\pi \int_0^\delta y(x) \sqrt{1 + y'(x)^2} dx \quad (13)$$

The boundary conditions are

$$y'|_{x=0} = 0; \quad y'|_{x=\delta} = \cot \theta \quad (14)$$

where  $\theta$  is the contact angle, which is given by Young's equation.

We non-dimensionalise the above system by defining

$$\bar{y} \equiv y/R; \quad \bar{x} \equiv x/R; \quad \bar{\delta} \equiv \delta/R; \quad \bar{A}_{d-l} = A_{d-l}/4\pi R^2; \quad (15)$$

Substituting these in and dropping the overbars,

$$\frac{2}{3} = \int_0^\delta y(x)^2 dx = \int_0^\delta H(x, y, y') dx \quad (16)$$

$$A_{d-l} = \int_0^\delta y(x) \sqrt{1 + y'(x)^2} dx = \int_0^\delta G(x, y, y') dx \quad (17)$$

$$y'|_{x=0} = 0; \quad y'|_{x=\delta} = \cot \theta; \quad (18)$$

It will now be argued that when the Helmholtz Free Energy of the *entire system* is minimised, the functional for the liquid-liquid area given by Eq. (17) will be stationary. As shown above, if the Helmholtz Free Energy is minimised, the following functional will be stationary:

$$\mathcal{J} = \gamma_{d-l} A_{d-l} + \gamma_{d-s} A_{d-s} + \gamma_{s-l} A_{s-l} \quad (19)$$

In the language introduced in this section,  $\mathcal{J}$  is a functional of  $y(x)$ . However, both  $A_{d-s}$  and  $A_{s-l}$  depend only on the endpoint  $y(x = \delta)$ , and not on the shape of the function itself. Hence if a variation is added to  $y(x)$  (to convert it to  $y(x) + dy(x)$ ) which satisfies  $dy(x = \delta) = 0$ , then the only term on the right hand side of Eq. (19) which will be affected is the first term involving  $A_{d-l}$ . Hence, the fact that  $\mathcal{J}$  is stationary under such variations implies that the functional  $A_{d-l}$  (which is given by Eq. (17)) is also stationary under such variations. This statement is strong enough to justify the application of the Euler-Lagrange equation below (see Gelfand and Fomin's *Calculus of Variations*).

Returning to the main argument: we now seek a function  $y(x)$  for which the functional  $A_{d-l}[y]$ , as given by (17), is stationary (at least among the class of functions with fixed end point at  $x = \delta$ ) and which satisfies (16) and (18). It may be shown via standard techniques that such a stationary point  $y(x)$  must satisfy the Euler-Lagrange equation with a Lagrange multiplier,  $\lambda$ ,

$$G_y - \frac{d}{dx} G_{y'} + \lambda \left( H_y - \frac{d}{dx} H_{y'} \right) = 0. \quad (20)$$

where  $G(x, y, y')$  and  $H(x, y, y')$  are as defined in Eq. (17) and (16). For these equations, this becomes

$$\sqrt{1 + (y')^2} - \frac{d}{dx} \left( \frac{yy'}{\sqrt{1 + (y')^2}} \right) + 2\lambda y = 0 \quad (21)$$

$$\sqrt{1+(y')^2} - \left( \frac{yy'' + (y')^2}{\sqrt{1+(y')^2}} \right) + \left( \frac{y(y')^2 y''}{(1+(y')^2)^{3/2}} \right) + 2\lambda y = 0 \quad (22)$$

$$\sqrt{1+(y')^2} - \left( \frac{yy'' + (y')^2 + yy''(y')^2 + (y')^4}{(1+(y')^2)^{3/2}} \right) + \left( \frac{y(y')^2 y''}{(1+(y')^2)^{3/2}} \right) + 2\lambda y = 0 \quad (23)$$

$$\sqrt{1+(y')^2} - \left( \frac{yy'' + (y')^2 + (y')^4}{(1+(y')^2)^{3/2}} \right) + 2\lambda y = 0 \quad (24)$$

$$(1+(y')^2)^2 - (yy'' + (y')^2 + (y')^4) + 2\lambda y(1+(y')^2)^{3/2} = 0 \quad (25)$$

$$1+(y')^4 + 2(y')^2 - (y')^2 - (y')^4 + 2\lambda y(1+(y')^2)^{3/2} = yy'' \quad (26)$$

$$1+(y')^2 + 2\lambda y(1+(y')^2)^{3/2} = yy'' \quad (27)$$

$$y'' = \frac{1+(y')^2}{y} + 2\lambda(1+(y')^2)^{3/2} \quad (28)$$

The two boundary conditions for this second order ordinary differential equation are:

$$y'(0) = 0; \quad y'(\delta) = \cot \theta; \quad (29)$$

However, these boundary conditions do not fully specify the ODE, as different solutions may be found for different values of the eigenvalue,  $\lambda$ . The appropriate value of  $\lambda$  will produce a solution  $y(x)$  which also satisfies the volume constraint:

$$\frac{2}{3} = \int_0^\delta y^2 dx. \quad (30)$$

It is clear that the Euler-Lagrange Equation (Eq. (28)), the two boundary conditions, and the volume constraint completely specify the shape of the compressed droplet,  $y(x)$ . In the next section, numerical solutions to the ODE-eigenvalue problem are presented. These solutions may then be used to calculate the force of compression via Eq. (6), which may be expanded to:<sup>2</sup>

$$F = -\frac{1}{2} \left( \gamma_{d-l} \frac{dA_{d-l}}{d\delta} + \gamma_{d-s} \frac{dA_{d-s}}{d\delta} + \gamma_{s-l} \frac{dA_{s-l}}{d\delta} \right) \quad (31)$$

By applying  $dA_{d-s} = -dA_{s-l}$  and Young's equation, this may be simplified to:

$$F = -\frac{\gamma_{d-l}}{2} \left( \frac{dA_{d-l}}{d\delta} - \frac{dA_{d-s}}{d\delta} \cos \theta \right) \quad (32)$$

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<sup>2</sup>Note that this equation is in dimensional form, and that it follows from Eq. (6) because  $l = 2\delta$ .

Defining the dimensionless force as  $\bar{F} = F/2\pi R\gamma_{d-l}$  and dropping all over-bars, we may write the dimensionless expression:

$$F = - \left( \frac{dA_{d-l}}{d\delta} - \frac{dA_{d-s}}{d\delta} \cos \theta \right) \quad (33)$$

Numerical values of  $F$  may be found by calculating  $A_{d-l}$  and  $A_{d-s}$  for multiple values of  $\delta$  and using a finite difference approximation to (32).

## 4 Numerical Solution

The second order differential equation, Eq. (28), can be written as a set of coupled first order DE's in  $(y_1(x), y_2(x))$ :

$$y_1' = y_2; \quad (34)$$

$$y_2' = \frac{1 + y_2^2}{y_1} + 2\lambda(1 + y_2^2)^{3/2} \quad (35)$$

The boundary conditions are:

$$y_2(0) = 0; \quad y_2(\delta) = \cot \theta \quad (36)$$

This ODE-BVP may now be solved numerically for various values of  $\lambda$ , however, in general, the solution  $y(x) = y_1(x)$  will not satisfy the constant-volume constraint:

$$\frac{2}{3} = \int_0^\delta y^2 dx. \quad (37)$$

A root finding algorithm may be used to find the eigenvalue,  $\lambda$ , which satisfies this constraint.<sup>3</sup> The code for this work may be found in the Jupyter Notebook `Plots For Capsule Compression.ipynb`.

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<sup>3</sup>In our implementation, values for  $y_1(0)$  and  $\lambda$  were guessed, and the non-stiff initial-value problem solver `Tsit5()` within the ODE library `DifferentialEquations.jl` in `Julia` was used to integrate (34) – (35) with  $y_1(0)$  equal to the guessed value and  $y_2(0) = 0$ . The sum of the squares of the residual error in the predicted values of  $y_2(\delta)$  (which should equal  $\cot \theta$  according to (36)) and in the volume constraint Eq. (37) were then minimised using a global minimisation algorithm (both the Nelder-Mead algorithm in `Optim.jl` and the Differential Evolution algorithms within `BlackBoxOptim.jl` worked well, though Nelder Mead converged faster and was surprisingly robust.)



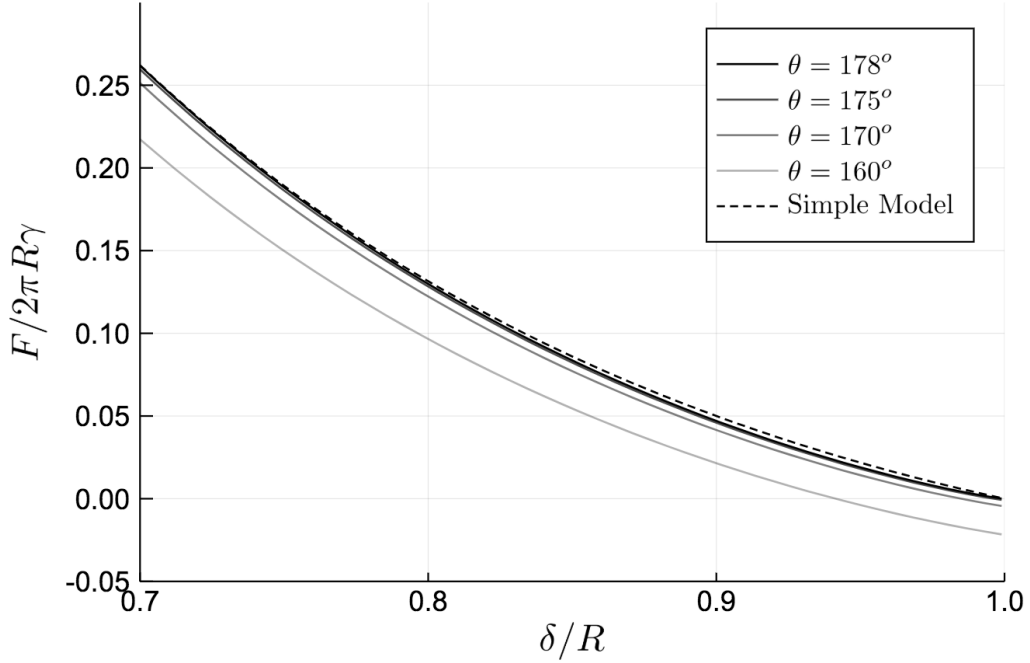


Figure 2: Compressive force vs degree of compression for droplets with various contact angles,  $\theta$ , and a second, idealised model.

## 5 Results and Discussion

In this section, dimensionless force curves are plotted for various values of the contact angle,  $\theta$ . In Figure 2, large compressions are shown (up to  $\delta/R = 0.7$ ) while in Figure 3 smaller compressions are shown. It may be seen in Figure 2 that if the contact angle is large, there may be an initial *attractive* force, as there will be a tendency to slightly wet the contacting solid surface. It may also be seen in Figure 2 that the very simple model developed previously provides a good fit, especially for larger compressions and contact angles. However, Figure 3 shows that this fit is less accurate for smaller compressions. In Figures 4-7, droplet profiles are shown for various contact angles  $\theta$  and degrees of compression,  $\delta/R$ . These profiles are all as expected.

### Appendix: Equations for Simple Model

The development of the simple model is described in the Word document ‘The Force Required to Reversibly Compress a Small’. In terms of the notation of

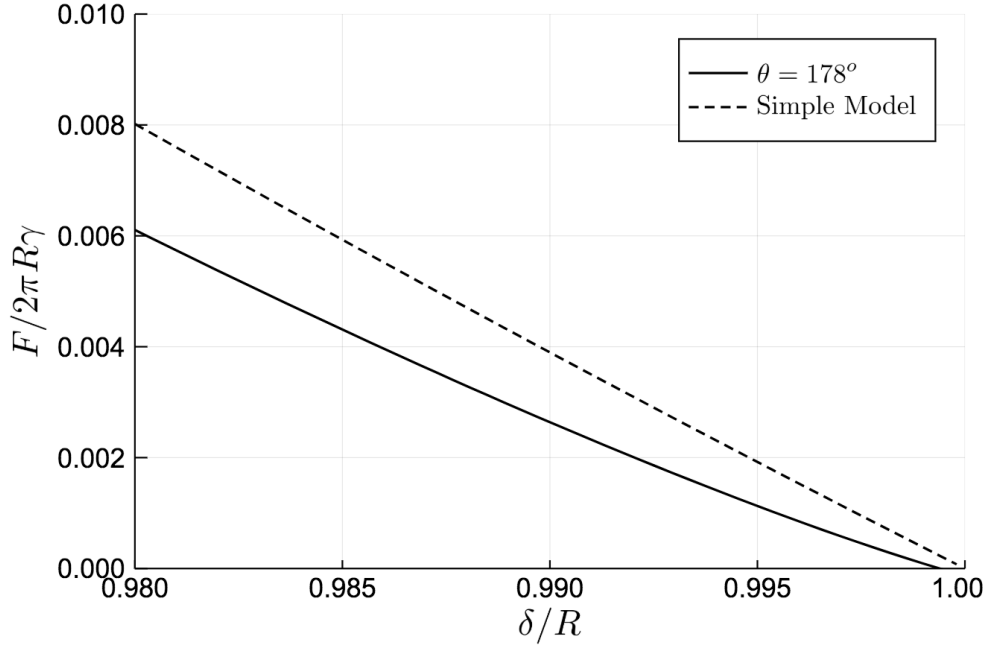


Figure 3: Compressive force vs degree of compression for small compressions..

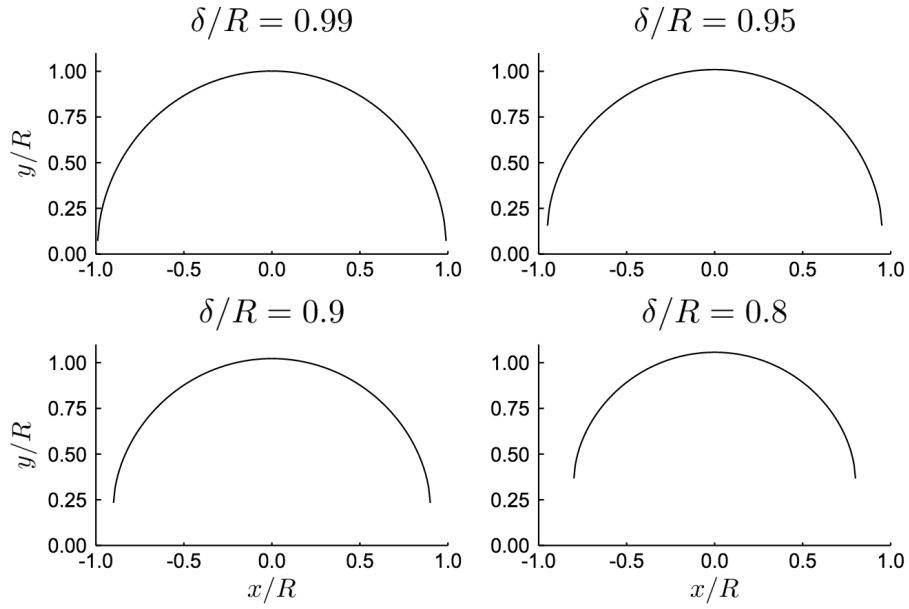


Figure 4: Profiles of compressed capsules with contact angle  $\theta = 178^\circ$ , for various degrees of compression.

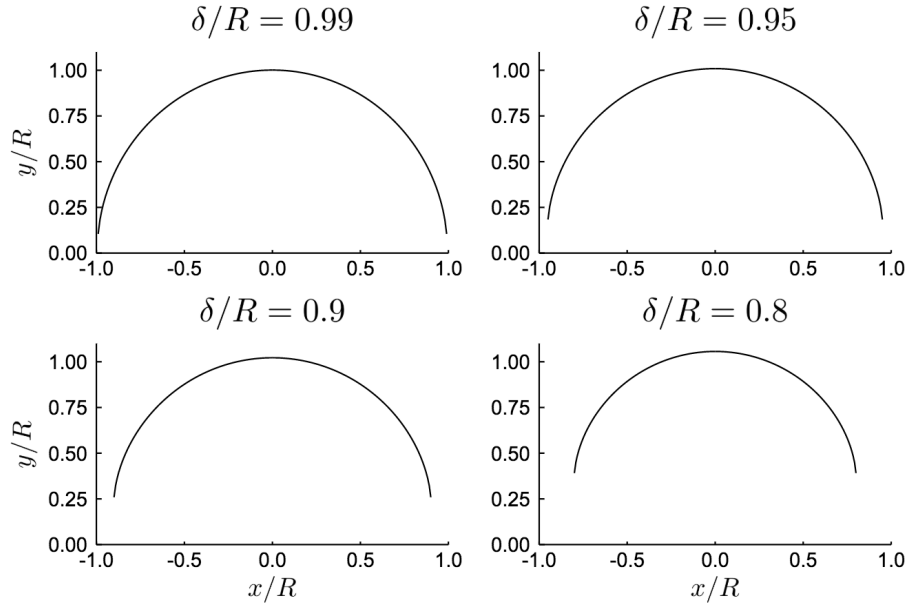


Figure 5: Profiles of compressed capsules with contact angle  $\theta = 175^\circ$ , for various degrees of compression.

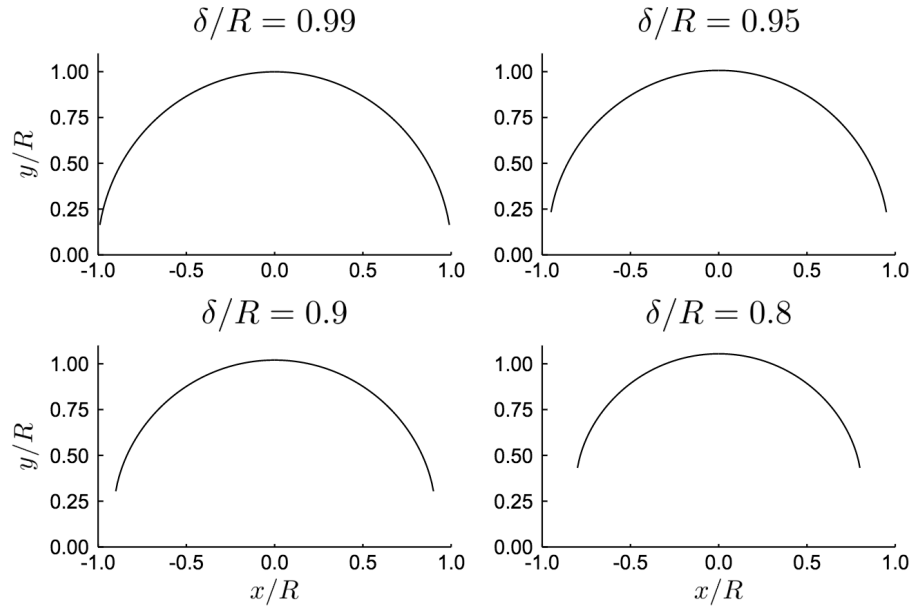


Figure 6: Profiles of compressed capsules with contact angle  $\theta = 170^\circ$ , for various degrees of compression.

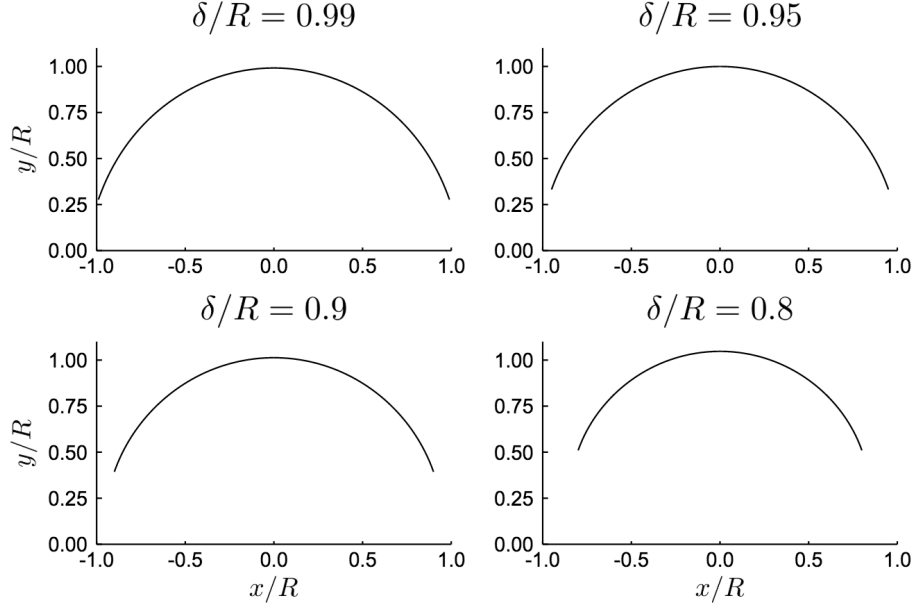


Figure 7: Profiles of compressed capsules with contact angle  $\theta = 160^\circ$ , for various degrees of compression.

the rest of this document, this model predicts, in dimensional form:

$$y(\delta) = -\frac{\pi\delta}{4} + \frac{1}{2}\sqrt{\frac{\pi^2\delta^2}{4} - \frac{8}{3}\delta^2 + \frac{8}{3}\frac{R^3}{\delta}} \quad (38)$$

$$A_{d-l} = 4\pi\delta^2 + 2\pi^2\delta y(\delta) \quad (39)$$

$$A_{d-s} = 2\pi(y(\delta))^2 \quad (40)$$

Non-dimensionalising according to the definitions given above and then removing the overbars,

$$y(\delta) = -\frac{\pi\delta}{4} + \frac{1}{2}\sqrt{\frac{\pi^2\delta^2}{4} - \frac{8}{3}\delta^2 + \frac{8}{3}\frac{1}{\delta}} \quad (41)$$

$$A_{d-l} = \delta^2 + \frac{\pi\delta y(\delta)}{2} \quad (42)$$

$$A_{d-s} = \frac{(y(\delta))^2}{2} \quad (43)$$

For a given value of  $\delta$ , we can calculate  $y(\delta)$  via (41) and then the areas via (42) – (43). The dimensionless force curve may then be calculated via Eq. (33) with  $\theta = 180^\circ$ , as the geometry of the model implicitly suggests this contact angle.