Consideration of the equilibrium of a droplet of liquid in contact with a **rigid** solid, surrounded by its vapour at constant pressure and temperature leads to the identification of a *contact* angle called the Young angle. In a closed system the equilibrium configuration is one that minimises the total energy of the system under the constraint of constant liquid volume (see figure 1).

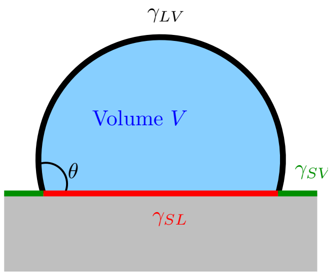

Figure 1: Liquid droplet in contact with an undeformable (rigid) solid substrate and vapour. The surface energies (in J/m^2) of the different interfaces are labelled, the contact angle θ is also labelled.

If the solid is assumed to be rigid the energy is the sum of the energies of the three interfaces solid-liquid (SL), liquid-vapour(LV) and solid-vapour (SV). Describe the liquid vapour interface as the graph $y = h(x)$ for $-L \le x \le L$, then the energy functional

$$E[h] = \gamma_{LV} \int_{-L}^{L} \sqrt{1 + h'(x)^2}\, dx + \gamma_{SV} \left(\int_{-D}^{-L} dx + \int_{L}^{D} dx \right) + \gamma_{SL} \int_{-L}^{L} dx \tag{1}$$

and the volume is $V = \int_{-L}^{L} h(x)\, dx$. Minimising the energy subject to this constraint gives the shape of the interface as an arc of a circle and the horizontal balance of configurational forces $\gamma_{LS} + \gamma_{LV} \cos\theta = \gamma_{SV}$, the solution of which gives the Young angle. The pressure inside the droplet is higher than that outside the droplet — the presence of the droplet alters the distribution of stress over the surface of the solid. If the solid is deformable the surface tension of the liquid-vapour interface will pull the solid upwards, whilst the droplet will push downwards, the two effects exactly compensate so that there is no overall force on the solid. Figure 2 illustrates the idea.

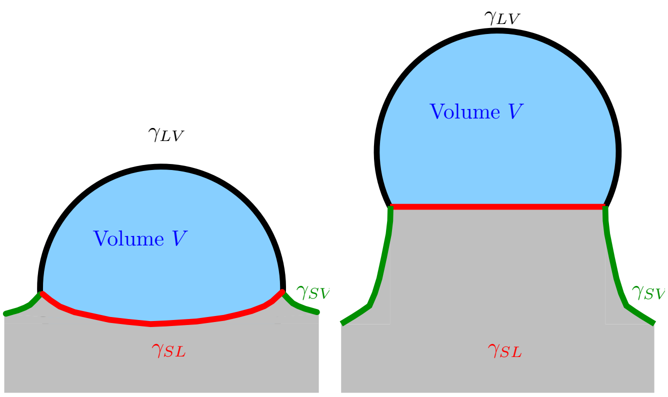

Figure 2: Liquid droplet in contact with an deformable solid substrate and vapour (left). Liquid droplet growing after deposition on substrate (right). The surface energies (in J/m^2) of the different interfaces are labelled. The action of a point/line force on an elastic substrate is the classical *Boussinesq problem*. Require a careful treatment the thermodynamics of elasticity and phase transformation.

The energy functional (1) must now include the deformation of the solid. If we represent the deformation gradient as $\boldsymbol{A}$, then a Green elastic material is defined by its strain-energy function W which is a function of the invariants of $\boldsymbol{A}$. Away from the contact point the strains are small and so a linearisation of the elastic part of the problem can be formulated and the behaviour of the solid is well approximated by the Boussinesq solution. Near the contact point the strains are large and finite elasticity must be used, restrictions are placed on the form of W for a solution to exist.

If the droplet can exchange mass with the solid (the liquid may be an alloy containing some of the pure/alloyed substrate), then a *chemo-mechanical* (compare with *thermo-mechanical*) equilibrium may be achieved. Interfacial, chemical and mechanical effects combine to produce an interesting coupled problem that may have some relevance to the the synthesis of certain nanowires (slender prisms of material that are 10–100nmwide and over 1µmlong). Certain nanowires are produced by using a catalyst droplet to crack molecules in the vapour that contain material that is absorbed in the liquid and deposited on the solid substrate (the Vapour-Liquid-Solid method). An understanding of the behaviour of liquid droplets in contact with solids is important in determining the growth and instabilities of wires grown in such a manner. Figure 2 illustrates the idea. Often during nanowire growth the droplet will be in contact with a solid which has corners (a faceted solid), what are the equilibrium shapes of droplets in such a configuration?

Approach Formulation of chemo-mechanical equilibrium [**??**] in the case of isotropic surface energy. This involves finite elasticity, the thermodynamics of alloys, some calculus of variations and modelling the materials. Some numerical work may be required to solve the coupled chemical–elastic problem. Anisotropic case — appropriate for crystal growth. Application to nanowire growth. What are equilibrium geometries of droplets? Are these relevant to growth?