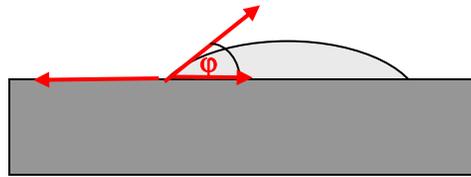


Wetting and Capillarity phenomena

The surface tension of liquids has familiar consequences on the contact geometry between liquids and solids or other liquids. In the absence of contact, the free liquid adopts a spherical shape, since this minimizes the area and thus the surface energy (drops and bubbles). If the surface tension of the liquid-vapor interface (γ) is smaller than the difference between that of the solid-vapor (γ_{sv}) and the solid-liquid (γ_{sl}), then the liquid is said to wet the surface and a flat film will form, because $\gamma + \gamma_{sl} < \gamma_{sv}$. If the sum is larger, energy is minimized by forming droplets that only partially cover the surface. The quantity $S = \gamma_{sv} - \gamma_{sl} - \gamma$ is called the spreading coefficient. For $S > 0$, the liquid spreads flat. For $S < 0$, droplets form that adopt spherical-cap shapes, with a contact angle ϕ .



The value of ϕ is determined by the condition of mechanical equilibrium of line forces (the contact line does not advance or recede). Since the forces are tangent to the corresponding interface planes and perpendicular to the line, we have:

$$\gamma_{sv} = \gamma \cdot \cos\phi + \gamma_{sl} \quad (30)$$

This is called the **Young equation**. For shallow droplets, (small contact angles) it can be rewritten as: $S = -1/2\gamma\phi^2$. We will use this expression later on.

The same result can be obtained by minimizing the total free energy as a function of droplet shape at constant volume. The minimization also shows that the shape is a spherical cap. This is of course neglecting other forces, in particular gravity. We shall come back to this subject later on.

The phenomena that are connected with the surface tension are called capillary phenomena. They include the above mentioned contact angle, as well as the capillary

raise or depression of liquids in narrow tubes against gravity forces, capillary waves, etc. Many of these manifestations have been used to experimentally determine the value of γ .

The disjoining Pressure

In the preceding discussion of the effects of γ the liquid films or droplets in contact with a solid or liquid surface were supposed to be macroscopic, or more precisely thicker than the range of the interaction forces with the surface. If the liquid film is very thin the energy of a molecule is not saturated since no other molecules of the same liquid exist beyond the interface surface. In other words, the free energy F (per unit surface), of the liquid in the film is different from that in the bulk material. As the film changes thickness, so does F . The thickness (z) variable has a conjugate one, in analogy with the pressure and volume where $p = -\partial F/\partial V$. So we have a new magnitude Π for thin films, defined by the relation:

$$\Pi = -1/A \cdot \partial F/\partial z \quad (31)$$

Π is called the disjoining pressure, and has dimensions of force per unit area. Π depends on z (in addition to other thermodynamic variables, such as T , etc.). As the film thickens to macroscopic values, Π obviously goes to zero. The disjoining pressure was introduced by Derjaguin, and is an important parameter to describe wetting phenomena of submicroscopic films.

The surface tension of an interface is a measure of the energy difference between fully coordinated atoms in the bulk and partially coordinated atoms near the surface. The forces of interaction between the atoms have a range that depends on the nature of the forces. For example they can be of very short range, $\sim 1\text{\AA}$ in chemical covalent bonds, or of tens or hundreds of \AA in electrostatic (ionic) type interactions. Electrostatic forces are rarely manifested by a full Coulombic dependence of the $1/r^2$ form except very close to the ion, because of polarization effects from other ions or from dipoles in the medium. For example, in ionic solids the field outside the surface decays much faster than $1/r^2$ due to the multipole assembly of lattice ions. In solutions, ions of the opposite charge

accumulate in the vicinity of the ions in such a way that the electric field is shielded, as in the Debye model used above.

Long-range Interaction forces between atoms and molecules

a. Dipole-dipole interactions

As an example of the interaction between neutral objects let's consider the dipole-dipole interaction. It is simple to show that the interaction energy of two dipoles with dipole moments p_1 and p_2 forming angles θ_1 and θ_2 with the line adjoining them is:

$$E(r, \theta_1, \theta_2, \varphi) = -\frac{p_1 \cdot p_2}{4\pi\epsilon_0 r^3} [2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\varphi]$$

where φ is the angle between the planes through the respective dipoles and connecting line. Dipoles with fixed orientations occur only in crystalline polar molecules. More often, due to thermal agitation the dipoles rotate quasi randomly. The average interaction energy in this case can be found by using Boltzman statistics, where a weight is assigned to each orientation according to the factor $\exp(-E(\theta_1, \theta_2, \varphi)/kT)$. We give here just the result of such averaging.

$$\langle E \rangle = \frac{\int E(\Omega) \cdot e^{-E(\Omega)/kT} d\Omega}{\int e^{-E(\Omega)/kT} d\Omega} = -\frac{\partial}{\partial t} \log \int e^{-E(\Omega)/kT} d\Omega$$

where $t \equiv 1/kT$. After integration over the θ 's and φ , only the second order term in the expansion of the exponential (which contains $(E/kT)^2$, assuming $E \ll kT$), gives a non-zero contribution. The thermally averaged energy (keeping r constant) is:

$$E(r) = -\frac{p_1^2 \cdot p_2^2}{3(4\pi\epsilon_0)^2 kT r^6}$$

This is called the Keesom interaction.

Exercise: calculate the order of magnitude of the Keesom interaction for water molecules.

b. The Van der Waals-London interaction

Another $1/r^6$ type interaction arises between neutral, non-polar atoms or molecules, due to “induced” dipoles, which is a purely quantum mechanical effect. This is the Van der Waals or London interaction. It is simple to deduce an expression for this interaction in the semiclassical picture of the Bohr atom. The electrons are “orbiting” around the nucleus and therefore there is an instantaneous dipole moment p_1 (\sim Bohr radius \times charge). This produces a field E_z component, which decays as $p_1/4\pi\epsilon_0 r^3$. In turn this field polarizes other atoms and induces in them a dipole $p_2 = \alpha E$, $\alpha =$ polarizability. The interaction energy is therefore:

$$E(r) = -\frac{p_1 \cdot p_2}{4\pi\epsilon_0 r^3} = -\frac{\alpha p_1^2}{(4\pi\epsilon_0)^2 r^6} = -\frac{C}{r^6}$$

The polarizability $\alpha = \frac{e^2}{m\omega^2} \approx 4\pi\epsilon_0 a_o^3$, can be related to the ionization energy by the

relation: $\hbar\omega = \frac{e^2}{2(4\pi\epsilon_0) \cdot a_o}$ (in MKS units).

Exercise: Calculate the order of magnitude of the forces. Using $\alpha \approx 4\pi\epsilon_0 a_o^3$, one gets $C \sim 3 \cdot 10^4 kT_{RT} \text{ \AA}^6$. For molecular distances of a few angstroms ($3.5^6 = 2 \times 10^3$), $E \sim 10kT$.

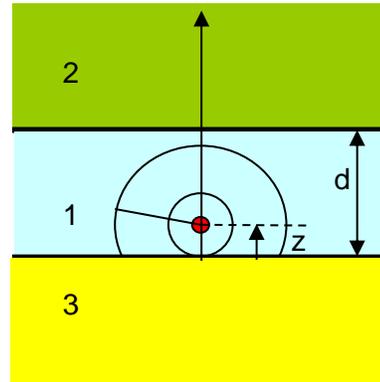
The quantum mechanical origin of E appears only through the use of the Bohr radius and polarizability, which contain Planck’s constant h . An elegant deduction of this interaction that brings the quantum effects in a clear way is given in Kittel’s Solid State Physics book. The interaction is the result of the decrease in the zero point energy of the interacting dipoles.

Another remark about the London force is that it assumes infinite propagation speed of the fields of the interacting dipoles. Since the speed of light is the maximum speed, it is clear that at sufficiently large distances ($r \gg c/v$) there will be a phase lag of more than 180° between the exciting field and reemitted field (photon) as it reaches the source. The effect of this is to decrease the strength of the interaction. This is the so-called retardation effect. Casimir and Polder [Phys. Rev. 73, 36 (1948)] showed that

retardation leads to a different distance dependence: $E \sim -C_{\text{ret}}/r^7$. So the exponent in the power law increased from 6 to 7 as the distance increases beyond the wavelength of the photons of freq. ν .

The Hamaker constant

In this section we will use a much simpler model to illustrate the origin and effect of unsaturated forces on the atoms near the surface. We will assume that particles interact with each other with $-1/r^6$ forces and that these forces are additive, an assumption which we know is not correct. In spite of this, the procedure gives surprisingly good results.



To analyze the effect of finite film thickness on its interaction with the surface we use the geometry shown in the figure. The total energy of a molecule inside medium 1 is:

$$E(z) := -C_{11} n_1 \int_a^z \frac{4 \cdot \pi \cdot r^2}{r^6} dr - C_{11} n_1 \int_z^{d-z} \frac{2 \cdot \pi \cdot r \cdot (z+r)}{r^6} dr - C_{11} n_1 \int_{d-z}^{\infty} \frac{2 \cdot \pi \cdot r \cdot d}{r^6} dr \dots$$

$$- C_{13} n_3 \int_z^{\infty} \frac{2 \cdot \pi \cdot r \cdot (r-z)}{r^6} dr - C_{12} n_2 \int_{d-z}^{\infty} \frac{2 \cdot \pi \cdot r \cdot (r-d+z)}{r^6} dr$$

where the first three terms represent the energy due to similar molecules in the film. The integration starts at $r = a$, the diameter of a molecule. The C 's are the constants in the van der Waals attractive energy terms. The n 's are the particle densities.

After all the integrations are done we get

$$E_{\text{total}} = -E_{\text{vol}} + \tilde{\gamma}_{12} \cdot S + \tilde{\gamma}_{13} \cdot S - \frac{H}{12\pi d^2}$$

Where: $\tilde{\gamma}_{12} = \gamma_{12} + \gamma_{21}$ and $\tilde{\gamma}_{13} = \gamma_{13} + \gamma_{31}$

The so-called Hamaker constant H is:

$$H = \pi^2 (n_1^2 C_{11} - n_1 n_2 C_{12} - n_1 n_3 C_{13} + n_2 n_3 C_{23})$$

It can be shown that: $C_{12} \approx \sqrt{C_{11}C_{22}}$, and similarly for C_{13} . The quantity: $v_1 = n_1\sqrt{C_{11}}$, is the index of refraction of medium 1.

$$H \cong \pi^2(v_1 - v_2)(v_1 - v_3)$$

Exercise: Orders of magnitude: C_{23} is of order $\sim 10^{-77} \text{ Jm}^6$, and the densities are $n \sim 10^{28} \text{ m}^{-3}$. Therefore, the Hamaker constant is $H \sim 10^{-19} \text{ J} \sim 0.1 \text{ eV}$.

Special cases:

a) $n_l = n_2 = 0$. This is the simple case of a free surface. The energy is simply:

$$E = -e.V + \gamma S \quad (\text{we dropped the indices})$$

b) $n_l = 0$. Two media (2 & 3) separated by vacuum.

$$E = E_{vol} + \gamma_2 S + \gamma_3 S - \frac{\pi^2 n_2 n_3 C_{23}}{12\pi d^2},$$

which is always an attractive force.

c) Thin film on a surface ($n_3 = 0$, vapor; solid, $s = 2$, liquid, $l = 1$):

$$E = E_{vol} + \gamma_{sl} S + \gamma S - \frac{H}{12\pi d^2}$$

The gammas are the solid-liquid and vapor-liquid surface tensions.

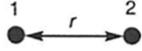
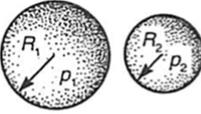
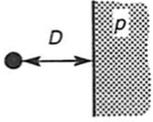
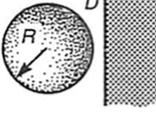
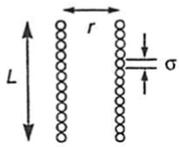
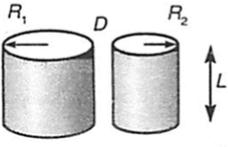
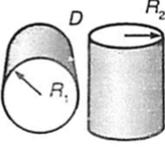
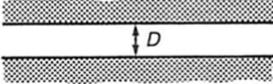
$$H = \pi^2(n_1^2 C_{11} - n_1 n_2 C_{12}) \cong \pi^2 v_l (v_l - v_2)$$

We have the following interesting result that if $v_1 > v_2$, i.e., if the liquid is optically denser than the solid, there is attraction between the surfaces. This means that the film is unstable against collapse (droplet formation) that brings the surfaces together in parts of the film, and of course far away in others to keep the volume constant. If on the contrary $v_1 < v_2$, the film is stable since the two surfaces repel each other. The film wets the solid surface. If one considers a solid covered by a liquid film of the same substance (like in melting), usually $v_1 < v_s$, so that the melt wets its solid. In the case

where $v_1 > v_s$, the liquid does not wet its own solid. However this result is not applicable to water, since the interactions are not properly described by a Van der Waals formula.

An interesting case is that where there are no forces between surfaces. This is convenient in AFM applications. A dielectric fluid with this property will suppress the van der Waals forces between tip and surface. The condition $H = 0$, is fulfilled for $v_1 = v_2$, or $v_1 = v_3$. For v_1 in between these two values, there is repulsion between tip and surface. For v_1 outside the two values, there will be attraction.

The result of the integration over the differently shaped volumes is shown in the figures, where $H = \pi^2 \cdot C \cdot n_1 \cdot n_2$ is the Hamaker constant. From Israelachvili's book (the book uses A instead of H for the Hamaker constant):

<p>Two atoms</p>  <p>$w = -C/r^6$</p>	<p>Two spheres</p>  <p>$W = \frac{-A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$</p>
<p>Atom-surface</p>  <p>$w = -\pi C \rho / 6D^3$</p>	<p>Sphere-surface</p>  <p>$W = -AR/6D$</p>
<p>Two parallel chain molecules</p>  <p>$W = -3\pi CL/8\sigma^2 r^5$</p>	<p>Two cylinders</p>  <p>$W = \frac{AL}{12\sqrt{2} D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$</p>
<p>Two crossed cylinders</p>  <p>$W = -A\sqrt{R_1 R_2}/6D$</p>	<p>Two surfaces</p>  <p>$W = -A/12\pi D^2$ per unit area</p>

Shape and thickness of microscopic liquid films

We are now ready to re-examine the wetting of liquids on solid surfaces which we discussed above for the macroscopic case, where surfaces and interfaces were characterized by their tensions (γ) alone. The macroscopic approach means that the size of the liquid film (thickness) or droplets (height) is larger than the range of the surface forces (up to $\sim 1000 \text{ \AA}$). Below that, the energy per molecule is not saturated to its bulk value, and if we use the bulk surface or interface tensions, we must correct for the surface forces. Pierre-Gilles de Gennes (1932-1997), Noble Prize in Physics in 1991, was one of the most influential scientists in developing the microscopic wetting theory.



Pierre-Gilles de Gennes

Surface forces give rise to the concept of disjoining pressure. We have seen forces originating from Van der Waals interactions that decay as $1/r^6$. We have seen that since there are three media involved, the disjoining pressure can be attractive or repulsive, depending on the value of the dielectric constants. Other forces besides Van der Waals can also be present, for example chemical and structural forces due to the short range interaction between molecules and between molecules and the substrate, electrostatic forces, “double layer” forces from solvated ions, hydrophobic and hydrophilic forces due to H-bonds, etc. A good discussion of the various surface forces can be found in the book of J. Israelachvili.

Sufficiently far away from the surface, when strong bonding forces have decayed to negligible values the Van der Waals force always remains. As we have seen, the potential energy is of the form:

$$P(z) = -\frac{H}{12\pi z^2},$$

The disjoining pressure in this case is:

$$\Pi(z) = \frac{H}{6\pi z^3}$$

which can be attractive or repulsive. The free energy of a surface covered by a thin film is then:

$$F(z) = \gamma_{sl} + \gamma + P(z)$$

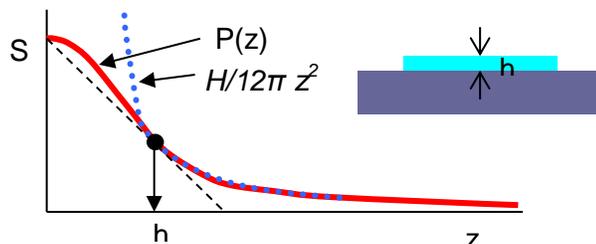
$P(z)$ is a decreasing function of z (in absolute value). In the limit when $z \rightarrow 0$ we must have $F(0) = \gamma_{sv}$, which is the solid-vapor surface tension. Therefore the limiting value of $P(z \rightarrow 0) = S = \gamma_{sv} - \gamma_{sl} - \gamma$, which is the spreading coefficient.

The shape of a thin liquid film on a surface depends on the sign of the two important magnitudes S and P . We have seen that if $P > 0$, the liquid-vapor and the solid-liquid interfaces “repel” each other or the disjoining pressure is positive (we have to press against the liquid surface to keep it from expanding). If $S > 0$, the film wants to spread. These two opposing tendencies equilibrate by the formation of a flat pancake of thickness, h . The value of h can be found by minimization of F at constant liquid volume $V (= Az)$:

$$F(z) = F_0 - A.S + A.P(z)$$

Minimization gives: $S = h.\Pi(h) + P(h)$

It is easy to see how to determine h graphically: it is determined from the tangent of a line through $(z=0, S)$ to the $P(z)$ curve:

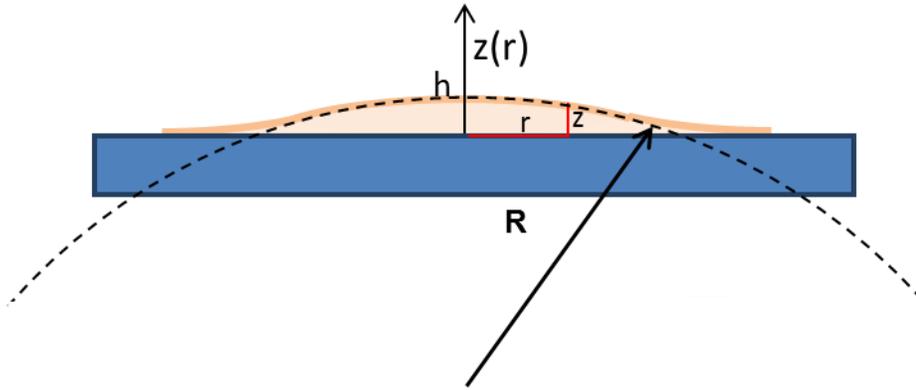


When non-wetting droplets form, their shape $z(r)$ that can be determined by minimization of:

$$F(drop) = F_0 + \int 2\pi r dr \left[-S + \frac{\gamma}{2} \left(\frac{dz}{dr} \right)^2 + P(z) + g(z) - \frac{\mu_{vapor} - \mu_{liq}}{v_{mol}} \cdot z \right]$$

This is the total free energy of the system, where the first term includes the energy of the dry surface (F_0), and the term S includes the energies of the dry part (not covered by the drop), the solid-liquid contribution (γ_{sl}) and the macroscopic value of the liquid-gas (γ) surface energies. The second term inside the integral is the correction for the liquid-gas area due to its curvature. $g(z)$ is the gravitational potential energy of the column of liquid, which is negligible in Nanoscale droplets and will thus be neglected here. The last term in the expression applies in the case where the droplet is growing in size due to condensation, but here we will assume no growth, i.e., $\mu_{vapor} = \mu_{liquid}$.

The equilibrium shape of the droplet is one that minimizes $F(drop)$ subject to the condition: $V = \int_{drop} 2\pi r \cdot dr = \text{constant}$.



The solution by the method of Lagrange multipliers requires numerical methods in general. We first create the function $f(r,z,z') = F - \lambda V$. (with $z' = dz/dr$). Where λ is the Lagrange multiplier.

The solution of the minimization problem is obtained from the Euler-Lagrange equation:

$$-\frac{d}{dr} \frac{\partial f}{\partial z'} + \frac{\partial f}{\partial z} = 0$$

Substituting we get: $P'(z) - \lambda = \gamma z'' + \gamma z'/r$, (I)

which can be integrated in z between z and h (top of the drop):

$$P(z) - P(h) - \lambda(z - h) = \frac{\gamma}{2} z'^2 + \gamma \int_h^z \frac{z'^2}{r} dr$$

(since the integral is over dz , we need to be replaced by $z'.dr$ in the terms that contain r explicitly).

In many experiments it is found that the shape of droplets is very close to a spherical cap, which is usually a very good approximation near the cusp (see AFM images in the example below). Therefore we will approximate the cusp of the droplet by a spherical cap of radius R , so that :

$$z'' = - (1+z'^2)/\sqrt{R^2 - r^2}$$

For $r \rightarrow 0$ this gives $z''(h) = -1/R$

We can get the value of λ from (I) in the limit where $r \rightarrow 0$: $P'(h) - \lambda = -\gamma/R$

Using this value of λ and inserting it into (I) we get:

$$P(z) - P(h) - \left(\frac{2\gamma}{R} + P'(h)\right)(z - h) = \gamma \int_h^z \frac{z'^2}{r} dr$$

The last integral, in the spherical cap approximation, is $-\gamma/R.(z-h)$.

We do not expect the drop to be a spherical cap near the edges, but we know that there $z'(r_{\text{edge}}) \sim 0$ (see figure below). So, we get finally for $z \rightarrow 0$:

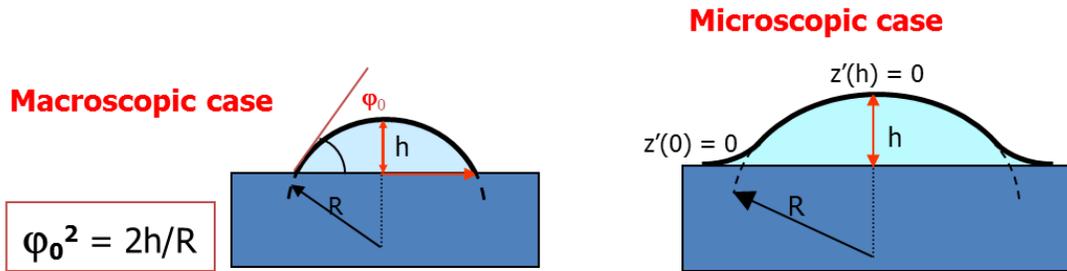
$$P(0) - P(h) + \left(\frac{\gamma h}{R} + h.P'(h)\right) = 0$$

We now use the relations: $\Pi(z) = -dP/dz$; and $P(0) = S = -1/2. \phi_o^2$, and by analogy we define $\phi^2 = 2h/R$, which is easier to measure in Nanoscale droplets (see figures below).

We then obtain finally:

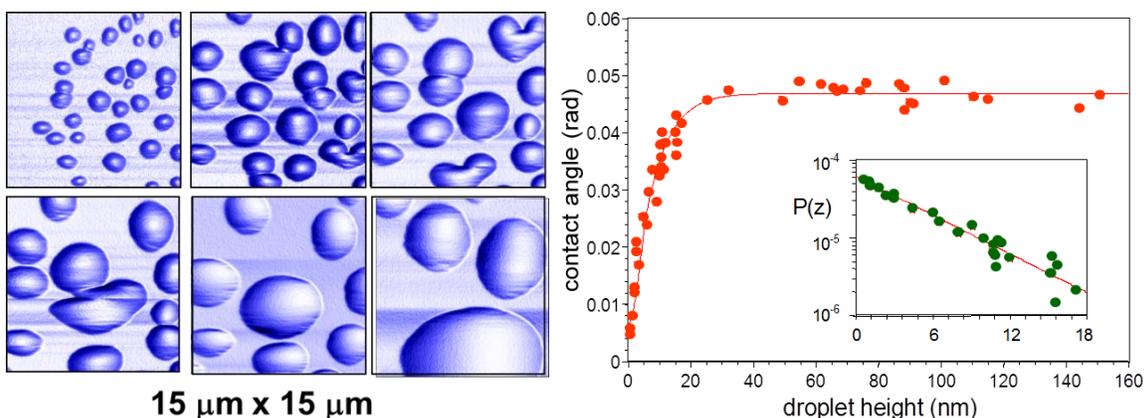
$$\varphi^2 = \varphi_0^2 + \frac{2}{\gamma} \cdot [P(h) + h \cdot \Pi(h)]$$

where φ is the Nanoscale contact angle of a droplet of height h and φ_0 = macroscopic contact angle. This formula predicts that the contact angle decreases as h decreases ($P, \Pi < 0$). This is to be expected since in this case the surface of the liquid and the solid “attract” each other, which tends to flatten the drop.



The example in the non-contact AFM figure shows the condensation of glycerol onto mica surfaces, made hydrophobic due to initial contamination. As the glycerol vapor condenses the droplets grow in size. The contact angle is measured in each droplet by fitting a sphere tangential to the cusp of each drop profile.

In a paper published in J. Phys. Chem. B 102, 7210 (1998), the authors used the measured ‘contact angle’ (from $2h/R$) as a function of droplet height to find the potential $P(z)$. Of the various forms examined, only the exponential dependence $P \sim -P_0 \cdot \exp(-z/d)$ gave a good fit, as shown by the semilog plot of $P(h)$ vs h in the inset. The fitting parameters were $d = 5 \text{ nm}$, and the strength of the potential at $z = 0$ (i.e., the spreading coefficient) $S = -6.4 \times 10^{-5} \text{ J/m}^2$. This gives a value for the negative disjoining pressure of $\sim 1 \text{ atm}$. The exponential dependence of $P(z)$ might be indicative of structural or hydrophobic attractive forces between the glycerol-air interface and the glycerol-mica interface.



This example clearly illustrates how by studying the wetting behavior, shape and size of nanoscale liquid films and droplets can provide a good understanding of the interaction potentials with substrates.

For interested readers, the classical books of A. Adamson, and by J. Israelachvili mentioned in the Syllabus provide extensive coverage of these topics.

Another very good book is by Pierre de Gennes, Françoise Brochard-Wyart and David Quere: “Capillarity and Wetting Phenomena”, published by Springer.

Other literature:

“Studies of wetting and capillary phenomena at nanometer scale with scanning polarization force microscopy”, by L. Xu and M. Salmeron. Chapter 6, pp.243-287 of the book “Nano-Surface Chemistry”, ed. By M. Rosoff. Network: Marcel Dekker, 2001.