CHAPTER 2

Experimental Techniques

Mechanical testing and imaging both play a central role in the scientific work presented in chapters 3-7. Here, we describe the different experimental techniques that were used in more detail.

2.1 Elastic modulus

When buying kiwis, avocados, mangos and many other types of fruit, people usually first squeeze the fruit a little to check how ripe it is. This works because the substances that hold fruit cells together break down and dissolve as the fruit ripens; fruit becomes softer as it ages. When fruit is squeezed, fingers apply a force on the surface area of the fruit: this is a compressive stress. In response to this stress, the fruit will deform and if the deformation is elastic the fruit will return to its original shape when you release the stress. The elastic modulus of the fruit is the ratio of stress to strain, where strain is defined as the deformation relative to the size of the object. Ripe fruit therefore has a lower elastic modulus than unripe fruit. To measure an elastic modulus, the strain response to an imposed stress, or the stress response to an imposed strain needs to be experimentally recorded. Depending on the geometry in which this is done, different moduli are measured. The shear modulus relates shear strain to shear stress. The Young’s modulus is measured when uniaxial stress and strain are applied. Below, we show how both moduli are measured in different systems.

2.1.1 Shear modulus of wet sand

The shear modulus is the ratio of shear stress to shear strain. Adding water to granular material like sand, has a big influence on the shear modulus of the
mixture[1], because liquid bridges can bind the grains together thereby increasing the stiffness of the mixture. In chapter 3 of this thesis, we investigate the effect of adding water to sand on the sliding friction on sand. We show that the shear modulus of sand/water mixtures is inversely proportional to the friction. A commercial rheometer is used for the modulus measurements; we insert the wet sand in a cup that is closed by the rheometer plate (Figure 2.1). The sand is compacted thoroughly before the upper plate is brought into contact with the sand surface for the measurement. The rheometer then imposes an oscillatory rotation on the upper plate, while no normal force is applied.

![Figure 2.1: A parallel plate measuring system. Sand mixed with water is inserted into the space between the parallel plates. The rheometer imposes an oscillatory rotation on the upper plate. Both the upper and lower plate are covered with sandpaper to avoid the sand from slipping over the plates. In the image, part of the cup is removed to show the space between both plates.](image)

The oscillatory rotation is defined by a frequency and an amplitude. The rheometer then measures the torque that is required to sustain this oscillation. To obtain the shear modulus from the measured and imposed parameters, the mean shear stress and shear strain are first calculated according to $\tau_m = \frac{4}{3\pi R^3} M$ and $\gamma_m = \frac{2\phi R}{3H}$, where $\tau_m$ and $\gamma_m$ are the mean shear stress and strain, $R$ is the radius of the upper plate, $M$ is the torque, $\phi$ is the deflection angle over which the upper plate rotates and $H$ is the distance between both plates. The shear modulus, $G$, is the proportionality factor that links the shear stress to the shear strain: $G = \frac{\tau}{\gamma}$. In Figure 2.2 we show the shear modulus that is obtained for a sand sample mixed with different amounts of water and measured using a 1 Hz oscillation with strain amplitude varying from 0.001 to 0.05.
2.1 Elastic modulus

The data shows that a small amount of water will increase the shear modulus of the water/sand mixture, but too much water causes the mixture to become muddy and therefore less stiff. At larger strain, the shear modulus decreases indicating that the deformation is not reversible anymore.

2.1.2 Young’s modulus of polytetrafluoroethylene

The Young’s modulus is the proportionality constant between uniaxial stress and strain. It plays an important role in contact formation, because surfaces are usually pressed together along one axis, the direction normal to the contact. In the experiments in chapters 4-6 we use sphere-on-flat contacts, because the real contact area between a sphere and a flat substrate is concentrated in a small region that can be viewed by microscopy. We also use sphere-on-flat contacts to measure the Young’s modulus. We compress a sphere between two plates using a Zwick/Roell Z2.5 tensile tester which controls the deformation through a stepper motor while measuring the force with a stiff force transducer. The materials that we have tested are generally three orders of magnitude stiffer than the sand/water mixtures discussed in the previous section. The stiffness of the samples is therefore not negli-
ble anymore, compared to that of the measurement system. To correct for any deformation that occurs within the components of the tensile tester that hold the two parallel plates in place, we first measure the deformation vs. force curve without a sphere between the two plates. The result is plotted in figure 2.3; for every Newton load the measurement system is compressed by 3 \(\mu\)m. We simply subtract this elastic deformation from the result that is obtained with the sphere in place.

![Deformation vs. Force Curve](image)

**Figure 2.3:** The deformation vs. force curve measured when no sample is inserted between the plates of the tensile tester. The finite compliance of the machine is 3.14 \(\mu\)m/N; this needs to be subtracted from the actual compression measurements.

A 3.14 mm polytetrafluoroethylene sphere is now inserted between the plates (Figure 2.4); the deformation \(\delta\) increases with the normal force \(N^{\frac{2}{3}}\). This is exactly what is predicted by Hertz theory\([2, 3]\) of elastic contact between a sphere and a flat substrate:

\[
\delta = \left( \frac{9N^2}{16RE^{*2}} \right)^{\frac{1}{3}}
\]

where \(R\) is the sphere radius and \(\frac{1}{E^{*}} = \frac{1-\nu^2}{E_1} + \frac{1-\nu^2}{E_1}\) with \(E\) the Young’s modulus and \(\nu\) the poisson ratio of the substrate and sphere material. The plate material, stainless steel for the upper plate and glass for the lower plate, is more than 100 times stiffer than PTFE. We can therefore ignore the
contribution of the two plates to $E^*$ which then simplifies to $E^* = \frac{E}{1-\nu^2}$, also known as the ‘plane-strain modulus’, which for most materials is only slightly lower than the Young’s modulus because $\nu$ is small. We squeeze the sphere between two plates, so there are two Hertzian sphere-on-flat contacts in the experiment each giving the same contribution to the total measured deformation which should then be:

$$\delta = \left(\frac{9}{2RE^*}\right)^{\frac{1}{3}} N^{\frac{2}{3}}$$

We fit this relation to the experimental data with $E^*$ as the adjustable parameter and find very good agreement for $E^* = 0.53$ GPa (Figure 2.4).

Figure 2.4: Deformation vs. force for a 3.14 mm PTFE sphere squeezed between two parallel plates. The compliance of the measurement system has been subtracted from the data. We fit the Hertzian relation between $\delta$ and $N$ to the data (see text) and obtain an elastic modulus of $E^* = 0.53$ GPa.

2.2 Penetration hardness

When a sphere is pushed into a flat substrate, the average contact pressure according to Hertz theory[2] is:
\[ P = \left( \frac{16E^*}{9\pi R^2} \right)^{\frac{1}{3}} N^{\frac{1}{3}} \]

Figure 2.5: Indentation of an ice surface with a 4.8 mm stainless steel sphere. At \(-12^\circ C\) the ice surface responds elastically to the sphere: the Hertzian relation between deformation and normal force is fitted to the data to obtain an elastic modulus of \(E^* = 0.84\) GPa. At \(-1^\circ C\) the ice yields to the sphere contact pressure, as indicated by the hysteresis in the loading/unloading curve. From the slope in the deformation vs. normal force curve we can now calculate the penetration hardness of the ice (see text): \(p_h = 7\) MPa

The contact pressure therefore increases with normal force and if the normal force is high enough, the sphere or substrate will yield. The penetration hardness is the maximum pressure that a surface can elastically support. In chapter 7, we show that the friction between a stainless steel sphere and an ice surface increases strongly when the contact pressure exceeds the penetration hardness. To measure this penetration hardness, we push the same stainless steel sphere into an ice surface using the tensile tester setup that was described in the previous section. In Figure 2.5 we plot the deformation of the ice surface vs. the normal force; the stainless steel sphere is more than 100 times stiffer and harder than the ice, so its contribution to the measured deformation can be ignored. At low temperatures, the behavior of the sphere on ice contact is elastic and the elastic modulus of the ice can be extracted by fitting the Hertzian relation between deformation and normal force to the data as before. At temperatures close to the ice melting point however, the
penetration hardness of the ice decreases and the contact transitions from elas-
tic to plastic. Elastic deformation is reversible, as illustrated in Figure 2.5, but
plastic deformation is not; when the sphere is retracted from the ice surface
after penetrating plastically, the surface does not ‘push back’ to return to its
original shape. The sphere-on-ice contact pressure is equal to the penetration
hardness of the ice during plastic contact: \( \pi r^2 = \frac{N}{p_h} \), with \( p_h \) the penetration
hardness of the ice and \( \pi r^2 \) the circular contact area. Since \( r^2 = 2R\delta \) for
\( \delta << R \), we can write \( \delta = \frac{N}{2\pi R p_h} \) and it follows that the slope \( \frac{\Delta \delta}{\Delta N} \) of the
plastic loading curve is inversely proportional to the penetration hardness:
\( \frac{\Delta \delta}{\Delta N} = \frac{1}{2\pi R p_h} \). At \(-1^\circ \text{C}\) we find a penetration hardness of \( p_h = 7 \text{ MPa} \).

2.3 Friction tests

The mechanics experiments described above ultimately serve to help us
understand contact formation and friction. To measure friction in the systems
that were mechanically characterized, we have transformed a commercial
tensile tester and a commercial rheometer into custom made tribometers,
both detailed in this section.

Figure 2.6: Friction experiments with a tensile tester. The tensile tester can
impose a speed and measure the force or impose a force and measure the speed.
We do sliding tests at constant speed by connecting a sledge to the tensile tester
using a rope and pulley system. The normal force is controlled by placing
weights on the sledge.


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2.3.1 Friction experiments with a tensile tester

The Zwick/Roell Z2.5 tensile tester is built to uniaxially stretch or compress materials, but it can also perform friction experiments. The sliding tests presented in chapter 3 were all recorded using the Zwick/Roell machine. In these experiments, we connect a PVC sledge with the tensile tester through a rope and pulley system as shown in Figure 2.6. The machine pulls on the rope to make the sledge slide over a substrate. The pull speed can be varied from $10 \mu m/s$ to $13 mm/s$ and the pull force is recorded with a resolution of $0.1 mN$. We control the normal force in this setup by placing weights on top of the sledge. In Figure 2.7, we show the friction measured between the sledge and dry beach sand from Zandvoort. The setup measures both static and dynamic friction. The friction coefficient, defined as the friction force divided by the normal force is 0.5 for this system.

![Figure 2.7: Friction of a PVC sledge covered with sandpaper sliding on dry beach sand. The slow initial increase in the friction force reflects the stretching of the rope. The peak friction force is the static friction that needs to be overcome to initiate the sliding. The constant dynamic friction force that follows is required to keep the sledge in sliding motion. The inset shows the static friction force vs. the normal force; the slope of this curve is the friction coefficient $\mu = 0.5$. All data was recorded at a sliding speed of $3.3 mm/s$.](image-url)
2.3 Friction tests

2.3.2 Friction experiments with a rheometer

Rheology is the branch of physics that deals with the deformation and flow of complex fluids. A rheometer is a mechanical testing device that is used to measure rheological parameters such as viscosity and complex modulus. Because the values of rheological parameters can vary over many orders of magnitude, rheometers need to measure and apply an enormous range of forces and deformations to a sample. The particular model we use (Anton Paar DSR 301), can vary the applied torque over nine orders of magnitude. This high level of precision makes rheometers very suitable for friction measurements; with a few simple changes, we convert our rheometer into a tribometer. All frictional data presented in chapters 5-7 was measured using this tribometer. To measure friction with a rheometer, we glue a sphere to the bottom of the measurement tool (Figure 2.8). The sphere can be brought into contact with the substrate by lowering the rheometer tool. The normal force is controlled by vertically displacing the tool with respect to the substrate; the stiffness of the rheometer-on-substrate system determines the precision with which the normal force can be set. The rheometer tool can be moved vertically with a precision of 1 \( \mu \)m. The normal force is measured by the rheometer with mN precision. As the tool is rotated, the sphere follows a circular path with radius \( a \). We divide the torque \( M \) measured by the rheometer by \( a \) to
obtain the friction force $F = \frac{M}{a}$.

In Figure 2.9 we plot the friction force measured between a 600 µm polystyrene sphere and a glass substrate. Both static and dynamic friction are obtained and we see that the friction grows sublinearly with the load; in chapter 5 we show that this is caused by strain hardening plasticity of the polystyrene surface.

Figure 2.9: The friction force between a 600 µm polystyrene sphere and a glass microscopy cover slip covered with a monolayer of covalently bonded rigidochromic molecules. The deflection angle is the angle over which the rheometer tool has rotated. The rotation rate of the rheometer tool translates into a sliding speed of 1 µm/s for the contact, each run lasts for 13 s. The static friction force is the peak friction value measured before the onset of slip. The dynamic friction force is the plateau value of the friction force. In the inset we plot the dynamic friction vs. the normal force. The friction coefficient is ill-defined because the slope of the data in the inset decreases with increasing normal force (see text).

**Full rotations**

The measurements presented in Figure 2.9 were taken at relatively low sliding speed and cover a total sliding distance less than 13 µm. To measure friction at higher sliding speeds, we simply increase the rotation rate of the rheometer. Because the rheometer will now make full rotations, we need to control the normal force in a different manner. The plane in which the sphere rotates is never perfectly parallel to the substrate. The sphere therefore usually makes
contact with the substrate only once during each full rotation (Figure 2.10a). The result is that automatically, a range of normal forces is sampled by the rheometer. In Figure 2.10b we plot the friction force vs. the normal force obtained in this type of experiment using a 4.8 mm stainless steel sphere on an ice surface. We see that \( F \propto N^{2/3} \), in chapter 7 we show that this behavior is expected if the contact is elastic and the friction is proportional to the contact area.

![Figure 2.10: The friction between a 4.8 mm stainless steel sphere and an ice surface. (a), Normal force vs. time. The sphere makes a full rotation every 150 s, it is in contact with the ice for about 20 s during each revolution due to the misalignment between the rotation axis and the substrate. The advantage is that a range of normal forces is automatically probed during each rotation. (b), Friction force vs. normal force measured during a single rotation. The inset shows an average of the same data. \( F \propto N^{2/3} \), this relation follows from Hertzian contact in which the friction is proportional to the contact area (see chapter 7).](image)

### 2.4 Microscopy imaging

The friction coefficient \( \mu \) is defined as the friction force divided by the normal force: \( \mu = \frac{F}{N} \). In the introduction of this thesis, we explain that since the work of Bowden and Tabor in the 1930s, the friction coefficient is considered to result from the fact that both \( F \) and \( N \) are proportional to the real contact area. To experimentally test the relation between normal force, friction force
and real contact area, we combine the friction tests described above with fluorescence microscopy of frictional contacts and atomic force microscopy of rough surfaces.

![Diagram](image)

**Figure 2.11**: Rheometer on confocal microscope setup. (a), The rheometer controls the normal and frictional force on a sphere-on-flat contact. A very smooth glass microscopy cover slip is used as the substrate. The rigidochromic molecules that are covalently bonded to the substrate surface can be excited from below with 488 nm laser light. The resulting fluorescence is captured by the microscope objective that is focused on the contact. We immerse the contact in dimethyl sulfoxide (DMSO) or formamide to avoid strong light scattering at the interface. (b), Rigidochromic molecules are covalently bonded to amino-functionalized glass microscopy cover slips using peptide coupling. Fluorescence deactivation of the rigidochromic molecule occurs via a twist around the $\beta$ bond[4]. This twist is prohibited within the contact area where the rigidochromic molecules are therefore fluorescent.

### 2.4.1 Fluorescence microscopy

The Anton Paar DSR 301 rheometer that is used for most of the friction experiments reported in this thesis, has a custom made frame that allows us to place the rheometer on top of an inverted microscope (Figure 2.11a). This enables us to simultaneously image and mechanically probe frictional contacts. A float glass microscopy cover slip is used as the substrate. We chemically attach a monolayer of ridigochromic molecules to the surface of these cover slips (see Figure 2.11b and chapter 4 for details). The microscope
is used in laser scanning mode, so that the rigidochromic molecules at the surface of the cover slip can be excited with 488 nm laser light. Rigidochromic molecules can decay to their ground state radiatively, or nonradiatively. The nonradiative decay path consists of rotations along specific bonds in the molecule that allow the charge that is displaced by the absorbed photon to return to its original position[4]. When the molecule is mechanically confined, for instance by a high viscosity liquid or a mechanical contact, some of the rotations involved in the nonradiative decay are prohibited. The molecule will therefore emit a fluorescence photon with a wavelength of roughly 540 nm to facilitate its return to the ground state; this is the radiative decay path. We focus the microscope on the contact area and then image the fluorescent light (Figure 2.12).

To calculate the real contact area between the sphere and the substrate based on the microscopy image, we first binarize this image using an Otsu [5] threshold (Figure 2.12). The number of contact pixels is then simply multiplied by the pixel area to obtain the real contact area.
Figure 2.12: The real contact area. (a), Original fluorescence image of the contact between a 600 µm polystyrene sphere and the glass substrate. Rigidochromic molecules remain dark in the background and only light up where there is contact. The contact force is 76 mN and the image size is 68 µm × 68 µm. (b), Binarized version of (a); the original image is thresholded and pixels with an intensity above the threshold are shown white. (c), Intensity distribution of the original image where the Otsu[5] threshold is shown in red. The real contact area is $4.7 \cdot 10^{-10}$ m$^2$ corresponding to an average contact pressure of 162 MPa.
2.4 Microscopy imaging

2.4.2 Atomic force microscopy

Figure 2.13: Atomic force microscopy. A very sharp silicon tip with radius less than 7 nm is brought into contact with the sample. The deflection of the cantilever is measured optically and using the cantilever stiffness of 0.2 N/m, the contact force associated with the measured deflection can be calculated. The tip raster scans the sample while it maintains a constant contact force. The contact force is held constant through a feedback loop between vertical position of the apparatus with respect to the sample and measured cantilever deflection. The result is a two-dimensional map of the sample surface heights.

In chapter 5, we compare the measured contact area (Figure 2.12) to that predicted by theory. Because the float glass microscopy cover slips onto which we press spheres are very smooth and stiff compared to the spheres, the theory only requires the sphere roughness and modulus as input. The measurement of the elastic modulus is described in the first section of this chapter. To measure the sphere roughness we use atomic force microscopy (AFM). In AFM, a sharp tip at the end of a cantilever is scanned over the sample while the deflection of the cantilever normal to the sample surface is measured optically (Figure 2.13). The cantilever has a known stiffness which allows for the calculation of the contact force from the measured deflection. For imaging of the roughness, we raster scan the sphere surface and measure the vertical displacement that is required to keep the cantilever deflection, or contact force, constant. Because the overall sphere curvature dominates the resulting height profile, we subtract this curvature from the raw data to obtain the roughness map (Figure 2.14).
Figure 2.14: AFM and fluorescence microscopy on the same sphere. (a), AFM image of the surface of a 600 µm polystyrene sphere. The sphere shape has been subtracted from the image. (b), Fluorescence image of the sphere from (a) in contact with a smooth rigidochromic cover slip at a contact force of 416 mN. The image is rotated and scaled to match the AFM image on the left. Identical surface details are visible in both experiments.
Bibliography


