Sliding friction
From microscopic contacts to Amontons’ law
Weber, B.A.

Publication date
2017

Document Version
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Molecular Probes Reveal Deviations from Amontons’ Law in Multi-Asperity Frictional Contacts

B.1 Experimental methods

B.1.1 Microscopy

Contacts were immersed in formamide to avoid strong light scattering at the interface and improve image quality. The experimental real contact area is taken as the number of contact pixels multiplied by the pixel area. Contact pixels are obtained from the microscopy images through intensity thresholding using the Otsu method. The contrast is such that contact and background fluorescence intensities hardly overlap and the threshold value is well determined (more details can be found in chapter 2).

Rigidochromic molecules fluoresce with an intensity that is proportional to the degree to which they are confined. Our molecules are grafted to the surface of glass cover slips with a density of roughly 80,000 molecules/µm², which we estimated by absorption spectroscopy (Figure B.1). We confirmed that the grafting density is homogeneous by imaging the fluorescence intensity of the cover slip surface immersed in formamide. The pixel area set by the laser scanning confocal microscope in typical contact experiments is 200 nm × 200 nm and should therefore contain roughly 3000 rigidochromic molecules.

The resolution with which the contact area can be resolved is limited by
Figure B.1: Absorbance, $A$, of rigidochromic cover slips was measured with a Shimadzu UV-2700 spectrophotometer. The absorbance of the sample functionalized with rigidochromic molecules was measured in air relative to the absorbance of glass cover slips functionalized with (3-aminopropyl)triethoxysilane, onto which the rigidochromic molecules used in our measurements are covalently attached. Because our samples only contain a single layer of chromophore molecules on the glass surface, absorbance values are very low and contain a significant amount of noise. In order to minimize the effect of noise on our measurements, we apply a Locally Weighted Scatterplot Smoothing (LOWESS) procedure[1] (red line). The absorbance assumes maximal value at 488 nm; 0.0016. Assuming that the optical cross-section (or molar attenuation coefficient, $\epsilon$) of immobilized molecules remains similar to the one measured for the same chromophore dissolved in toluene ($\epsilon_{\text{max}} = 62200 \text{ cm}^2/\text{mmol}^{-1}$)[2], one can estimate the grafting density of $\frac{A}{\epsilon} \sim 80,000$ molecules/µm$^2$.

the microscope point spread function (PSF). To measure this PSF, we image a single 100 nm fluorescent bead under the same optical conditions as those applied in the contact experiments. The image of the point source is radially averaged around the center of intensity to obtain a Gaussian profile with full width at half maximum of 450 nm (Figure B.2). Simulations based on the sphere surface profile measured by AFM have a higher resolution. We convolute the simulation results with the microscope PSF to obtain contact images that can be directly compared to experiment.
Figure B.2: Radially averaged intensity distribution around the center of a point source. The image is recorded using the hardware and settings that were used for contact imaging. The distribution of pixel intensities in the image as a function of distance from the center of intensity is plotted. The profile is approximately Gaussian with a full width half maximum of 450 nm.
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Figure B.3: Fluorescence intensity and average photon arrival time at the PS on rigidochromic glass contact. a) Fluorescence intensity image of the edge of the contact. b) Average photon arrival time image corresponding to panel a). Both fluorescence intensity and photon arrival time are relatively homogeneous within the contact area; the plastic deformation of the PS surface likely results in full contact, also at unresolved length scales. The average photon arrival time at the contact is 1.3 ns, lower than the 2.5 ns[6] typically found when the molecule is trapped in bulk polymer matrix. If the PS surface is indeed softer[7, 8] than the bulk, as the contact simulations indicate, a lower photon arrival time is expected. Fluorescence decay curves of the monolayer of rigidochromic molecules on cover slips were measured using a different microscope than the other data reported here: a MicroTime 200 confocal microscope (PicoQuant GmbH) with a 100x 1.4 NA objective (UplanSApo, Olympus), mounted on a piezo-scanning stage (Physik Instruments GmbH). A detection pinhole with a diameter of 50 µm was used. NKT SuperK Extreme white continuum pulsed (25 MHz) laser was used for excitation.

The average photon arrival time, defined as the time between excitation of the molecule and emission of a fluorescence photon, is an independent measure of the degree to which rigidochromic molecules are confined at the contact. We resolve the contact area of a polystyrene (PS) sphere pressed onto glass in a fluorescence lifetime imaging microscope (Figure B.3). The average photon arrival time within the contact of 1.3 ns indicates that the environment of rigidochromic molecules at the interface is less rigid than that measured in bulk polymer[6], 2.5 ns. Indeed polymer surfaces are known to be softer than bulk[7, 8]. The hardening simulation (main text) hints at the same behavior; the PS surface layer is plastically deformed at stresses that would not make bulk PS yield.

The sublinear relation between contact area and contact force causes the
Figure B.4: Fluorescence intensity and contact pressure. The average contact pressure is defined as the contact force divided by the contact area resolved by microscopy. The average contact intensity is defined as the total fluorescence intensity divided by the same contact area. The background intensity is subtracted. Data is shown for a PS sphere that did, and one that did not undergo the roughening treatment as well as a PMMA sphere like that presented in chapter 4.

average contact pressure to vary. In general, the fluorescence intensity can go up due to the number of confined molecules or the degree of confinement. In Figure B.4, we plot the average fluorescence intensity per unit contact area vs. the average contact pressure. If the increase in fluorescence intensity with pressure were due to an increase in the number of confined molecules, i.e. the real contact area at length scales that are not resolved by the microscope, we would expect the intensity to rise roughly linearly with pressure. Instead, we observe that the fluorescence intensity is proportional to the square root of the pressure. This behavior is consistent with an increase in the degree of confinement while the number of confined molecules has saturated; we observe a very similar relation between pressure and fluorescence intensity when we immerse rigidochromatic molecules in a hydrostatically compressed liquid (see chapter 4). The contact simulations, based on AFM data with a lateral resolution of 32 nm rather than the 450 nm of the microscopy PSF (see Figure B.5), support this conclusion since they do not contain more contact structure than the microscopy images.

In the contact experiments, a small fraction of the 488 nm excitation light
Figure B.5: Hardening simulation of the real contact area from the main text with (a) and without (b) application of the microscopy point spread function. The resolution of the AFM data is 32 nm, rather than the 450 nm obtained through microscopy. However, the simulation based on the high resolution AFM data does not show contact area structure that is not resolved by the microscope; all small scale roughness is flattened by the contact pressure.

gets reflected by the interface between the sphere and the contact immersion liquid or the substrate and the contact immersion liquid. The interference between these two contributions leads to a ring shaped intensity pattern around the contact, commonly known as Newton rings (Figure B.6). These rings have maximal intensity where the gap between the sphere and the substrate is equal to:

\[
d = \left( m + \frac{1}{2} \right) \frac{\lambda}{2n}
\]

where \( m = 0, 1, 2, 3 \ldots \) is the ring number, \( \lambda = 488 \text{ nm} \) is the wavelength and \( n = 1.447 \) is the refractive index of formamide. We consider a line profile that runs through the center of the contact and extract the points at which the line intersects with the Newton rings. Using the gap from Eq. (B.1), these intersection points then give us the profile of the gap between the sphere and the substrate, close to the contact (Figure B.7). By extrapolating this profile towards the edge of contact, as indicated by the fluorescence signal, we obtain the gap at which the rigidochromic molecules light up (Figure B.7). 20 different profiles were taken, leading to an average gap
B.1 Experimental methods

Figure B.6: Fluorescence (green) and reflections (blue) measured at the contact between a 4 mm glass sphere and a rigidochromic cover slip (image size: 90 μm × 90 μm). For the fluorescence imaging we use the same setup and settings as reported in the main text. For the imaging of reflections we remove the beamsplitters and filters that block reflected light and replace them with a filter that blocks the fluorescent signal. The red line crosses the center of the contact as well as the Newton rings around it. The smallest ring indicates a gap of 84 nm between the sphere and the cover slip.

of 9 nm between the sphere and the substrate at the location where the fluorescence intensity image indicates the edge of the contact. Because the Newton rings give the average local gap, while the rigidochromic molecules measure the minimum local gap, 9 nm is an upper limit on the distance between the two surfaces at which the rigidochromic molecules light up. Indeed the combined roughness of the precision sphere and the float glass cover slip used for this measurement is typically of the same order. In comparison to frustrated internal reflection used for contact detection in other experiments[10], rigidochromic molecules are therefore more than an order of magnitude more sensitive. Figure B.6 shows what the consequence is for the measured contact area: the area within the first Newton ring represents gaps smaller than 84 nm, roughly the sensitivity of frustrated internal reflection measurements[10], the fluorescent area is roughly four times smaller.
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Figure B.7: Intensity profile and gap extrapolation. a) The fluorescence (green) and the reflections (blue) along the line profile in B.6. Blue circles indicate the positions of maximum intensity for each Newton ring. The Otsu fluorescence intensity threshold that separates contact pixels from background pixels is given by the dashed line. The green squares give the edge of the contact defined by the Otsu threshold. b) The gap of each Newton ring calculated using Eq. (B.1) and plotted vs. the distance from the contact center as obtained from a). By fitting a second degree polynomial to the rings, we calculate the gap at the edge of the contact, as it is observed using the fluorescent molecules. Averaging over 20 different profiles we obtain a gap of 9 nm. This sets an upper limit to the distance at which a rigidochromic molecule lights up due to contact (see text).

B.1.2 Mechanical testing

Roughening

PS spheres were inserted in a container with 240 grit sandpaper walls and then shaken for at least 8 hours to obtain a roughened surface. poly(methyl methacrylate) (PMMA), polytetrafluoroethylene (PTFE) and glass spheres were not roughened prior to the experiments.

Elastic modulus

The PS and PMMA plain strain moduli $E^*$, were measured using the procedure described in chapter 2 for PTFE. We find $E_{PMMA}^* = 3.5$ GPa and $E_{PS}^* = 3.7$ GPa. We also confirmed that the experimental contact radii agree with the Hertzian contact radii calculated using these values (see chapter 4).
Friction

During friction tests, the rheometer measures the torque on the plate to which the sphere is glued (see chapter 2 for more details). We calculate the friction force from this torque using the rotation radius of the sphere, measured by microscopy. This radius can be determined with 1% accuracy and is typically two orders of magnitude larger than the size of the contact. The same radius is used to calculate the sliding speed and distance. Friction tests were performed on dry float glass. Similar results are obtained when we wet the contacts with formamide.

B.2 Numerical contact models

B.2.1 Greenwood & Tripp model

The asperity radius $B$ for the Greenwood & Tripp (GT) model[11] is obtained from the root mean square curvature $h''_{\text{rms}}$ of the measured rough surface, $B = 1/h''_{\text{rms}}$. The asperity density $\eta$ is approximated by the relationship[12, 13] $\eta h_{\text{rms}} B \approx 0.05$. The GT model then yields the roughness-averaged surface deformation profile. Contact area and geometry are obtained from the bearing area approximation: spots where the rough profile penetrates this deformation profile are in contact.

B.2.2 Elastic interactions

We model normal elastic contact between two surfaces with discretized topography maps $h^{(1)}_{xy}, h^{(2)}_{xy}$, where $xy$ denotes the in-plane coordinate. This can be mapped exactly onto a rigid rough surface of height $h_{xy} = h^{(1)}_{xy} - h^{(2)}_{xy}$ and a deformable elastic solid of contact modulus $E^*$. For the PS and PMMA on glass contacts, $E^*$ is directly measured in a tensile tester. The topography maps of the glass and polymer surfaces are obtained using AFM. The glass roughness is ignored in the simulations, because it is negligible compared to that of the polymer surface.

The linear elastic response of the contacting surface is numerically calculated using an efficient Green’s function technique that considers just the normal displacement of the surface. This approach ignores lateral interfacial slip during contact but is the exact numerical solution of the model that Greenwood-Williamson’s and Persson’s theory approximate. In brief, we use the Green’s functions obtained for an isotropic linear elastic half-space subject
to a constant normal load distributed over square patches[14] and accelerate
the convolution using a fast Fourier transform (FFT) technique[15, 16, 17].
The calculation is supplemented by a padding region that cancels any effect
from repeating images of the FFT[18, 19]. The interface between the two
surfaces is treated as impenetrable hard walls[20]. These calculations give
the displacement $u_{xy}$ (positive pointing into the deformable substrate) and
pressure $p_{xy}$ on a square numerical grid across the contacting interface.

**B.2.3 Plasticity models**

All plasticity models considered are local evolution laws for the plastic dis-
placement $h_{xy}^{pl}$. $h_{xy}$ is updated iteratively while the two surfaces are brought
into contact. The full deformed topography is then $h'_{xy} = h_{xy} + h_{xy}^{pl}$. The
penetration hardness model solves for the elastic deformation imposed by a
contacting (and potentially deformed) topography $h'_{xy}$, but adds an upper
limit[21] on the local pressure $p_{xy}$. This limiting pressure is the penetration
hardness $p_Y$. Numerically, this is implemented by modifying Polonsky &
Keer’s constrained conjugate gradient solver[20] to optimize the pressure $p_{xy}$
only in regions where $p_{xy} > 0$ and $p_{xy} < p_Y$ and keep it bounded to 0 and
$p_Y$ otherwise. The gap $g_{xy} = u_{xy} - h_{xy}$ is positive where $p_{xy} = 0$, negative
where $p_{xy} = p_Y$ (and the material deforms plastically) and zero otherwise.
Negative gaps $g_{xy}$ define the plastic increment; in the simplest case

$$\Delta h_{xy}^{pl} = g_{xy} \theta(-g_{xy})$$  \hspace{1cm} (B.2)

where $\theta(x)$ is the Heaviside step function. We use simple overrelaxation to
solve for the plastic deformation: the surface is deformed by a fraction $\alpha$ of
the plastic increment, $h_{xy}^{pl} \rightarrow h_{xy}^{pl} + \alpha \Delta h_{xy}^{pl}$. We iterate elastic computation
of the gap $g_{xy}$ and relaxation of $h_{xy}^{pl}$ until the gap $g_{xy}$ becomes non-negative
everywhere in the simulation domain.

Note that the plastic increment given by Equation (B.2) is not volume
conserving but has the advantage that $h_{xy}^{pl}$ can be computed in a single
iteration without relaxation ($\alpha = 1$). A volume conserving increment needs
to fulfill $\sum_{xy} \Delta h_{xy}^{pl} \equiv 0$. The simplest construction is a distribution of the
deformed volume to neighboring grid points,

$$\Delta h_{xy}^{pl} = [g_{xy} - (g_{x+1,y} + g_{x-1,y} + g_{x,y+1} + g_{x,y-1})/4] \theta(-g_{xy}),$$  \hspace{1cm} (B.3)

but this necessitates overrelaxation, $\alpha < 1$. We carried out penetration
hardness calculations with both formulations of the plastic increment, Equa-
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In the contact hardening model, we introduce a spatially varying \( p_{Y,xy} \) and adjust it locally according to \( h_{pl}^{xy}, p_{Y,xy} = kh_{xy}^{pl} \).

The penetration hardness model introduces a sharp cutoff in the pressure distribution at \( p_Y \) that is not present in the contact hardening model. The former is however consistent with results from full finite-element models using standard \( J_2 \) plasticity\cite{22} with isotropic hardening in the subsurface bulk of the materials. Calculations show that the surface pressure distribution is cut off by the plastic deformation and that the contact area is proportional to the applied load\cite{23}. We conclude that our polymers do not behave like \( J_2 \) solids. This can have multiple reasons, such as the well-documented pressure dependence of the yield stress of glassy polymers\cite{24} or a different mechanical behavior of the surface region\cite{25, 26}.

### B.2.4 Comparison with experiments

The final contact maps shown in Figures 5.2, B.8 and B.11 display regions where \( g_{xy} \equiv 0 \), convoluted with the PSF of the microscope. This facilitates comparison with experimental optical images that are always resolution-limited. We note that both contact models contain a single material parameter, the penetration hardness \( p_Y \) or the hardening coefficient \( k \). Figure B.8 compares the results obtained from experiment with penetration hardness and contact hardening models at varying parameters.

These results show that decreasing the penetration hardness or hardening coefficients makes the contact patches more compact and increases contact area. While the coarse details of the experimental contact geometry are reproduced by all calculations, only the contact hardening model correctly describes the finer details of the contact features and - most importantly - the deviation from linearity in the load vs. area curve shown in Figure 5.3.

As an independent test of the contact plasticity model, we show the plastically deformed surface \( h'_{xy} \) obtained from the contact hardening model alongside AFM measurements before and after contact in Figure B.9.

Clearly, the contacting region is flattened in the experiments and the overall magnitude and location of the flattened patches is well-described by the contact hardening model.

Next, we address the question if the nonlinearity in area vs. load is an effect of the sphere curvature. At low loads, the elastic contact of rough spheres behaves like the contact of a nominally flat rough surface (Ref. [18]...
Figure B.8: The real contact area at a normal load of 200 mN as a) measured and predicted by the b) penetration hardness and c) contact hardening models. The model calculations have been carried out for varying values of penetration hardness $p_Y$ and hardening coefficient $k$. Best agreement with experiment is obtained for the parameter set indicated by the blue rectangle.

To confirm this behavior for the contact hardening calculations, we calculate the contact of nominally flat, periodic surfaces for comparison. Because experimental surfaces are not periodic, we use synthetic, self-affine[27] surfaces that were generated using a Fourier-filtering algorithm[28] to avoid edge effects. The elastic deformation of the substrate is computed using the continuum Green’s function for periodic systems[29, 30, 15]. Red lines in Figure B.10 shows the result of these calculations. There is no difference in the results obtained for nominally flat (solid lines) and curved (broken line) surfaces. Both cases show identical power-law scaling of area with load, demonstrating that the curvature of the interface does not change the macroscopic contact law.
Figure B.9: AFM imaging of the sphere surface a) before and b) after it is pushed into contact with the functionalized glass substrate. The circular region of contact, indicated in b), has clearly been permanently deformed during the contact experiment, while regions outside of this circle have maintained their roughness. Panel c) shows the results of the contact hardening calculation. The extent of the plastic deformation of individual contact patches is in good agreement with the deformation measured in experiment. Sphere curvature was subtracted from the raw AFM and simulation data.

Figure B.10: Contact of a synthetic self-affine surface with Hurst exponent 0.8 on flat (colored solid lines) and curved (broken lines) interfaces. Solid black lines indicate linear and Hertzian (2/3 power law) behavior. The curvature radius shown here is $R = 50,000 \lambda_s$, where $\lambda_s$ is the shortest wavelength with nonzero power. Simulations were carried out on a grid of dimension $2048a_0 \times 2048a_0$ ($a_0$ is the grid spacing) and $\lambda_s = 2a_0$. There is no difference between flat and curved interfaces for both elastic and contact hardening calculations. This demonstrates that the power-law observed in contact-hardening calculations is due to the hardening law, not the sphere curvature.

### B.3 Other materials

The demonstrated strain hardening contact mechanics does not only occur in PS. A 1.5 mm PMMA sphere was brought into contact with a rigidochromic
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Figure B.11: The real contact area between a rough 1.5 mm PMMA sphere and a flat rigidochromic cover slip measured and simulated at increasing loads. a), Fluorescence intensity images of the contact geometry. b), Purely elastic simulation. c), Elasto-plastic contact hardening simulation with hardening modulus \( k \approx 7 \text{ MPa/nm} \). Simulations use the sphere profile measured by AFM before the contact experiment as input. The elastic moduli and Poisson ratios of the PMMA and the glass were measured using a tensile tester (see chapter 2). Simulated contact geometries are convoluted with the optical point spread function.

cover slip. Like with the PS spheres, an AFM scan of the sphere surface was recorded prior to the contact experiment. The measured roughness profile, together with the elastic modulus measured using the method described above, were used as input for contact calculations (Figures B.11 and B.12). The results support the exact same conclusion that was drawn from the PS case: the real contact area can only be predicted by a mixture of long-range elasticity and short-range hardening.

Deviations from Amontons’ law were not only found for the PS spheres. Tests with PTFE, PMMA and glass show (Figure B.13) that both contact area and static friction grow sublinearly with the contact force.
Figure B.12: The contact mechanics of a rough 1.5 mm PMMA sphere. Symbols show experimental values and solid lines show values obtained from theory, using the surface roughness measured by AFM as input. Experimental contact is reproduced by the contact hardening model that considers long range elastic asperity interactions and local plasticity at contact. The penetration hardness model and the purely elastic model underestimate the contact area or do not describe the deviation from linearity found in the experiment.

Figure B.13: Deviations from Amontons’ law in 3.14 mm PTFE, 0.6 mm PS, 4 mm PMMA and 4 mm borosilicate glass spheres. a) The sublinear relation between contact area and normal force analyzed for PS spheres in chapter 5 is also observed using different sphere materials. b) The static friction is roughly proportional to the contact area for all materials, resulting in a deviation from Amontons’ law. All contact and friction data was normalized to the contact area and friction force measured at 25 mN.
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Bibliography


