Chapter 6
Frictional Properties of Pinned-Micelle Polymer Monolayers

Friction force measurements were performed on pinned-micelle monolayers. We found a linear dependence upon the applied load and the shear velocity, implying multiasperity contact and “viscous” friction, respectively. The friction coefficient while it was found to compare well with the friction coefficient of bulk polystyrene that has been reported in the literature, is 33% higher than the local friction coefficient $\mu_0$ for PS globules that was found in the previous chapter. This difference is attributed to adhesion differences in connection with topography.

6.1 Introduction

Several models make predictions about the functional dependence of (shearing) friction as a function of normal force. We will briefly discuss the most relevant ones to our system. The Amonton’s law states that the friction force $F$ is proportional to the normal load force $F_l$. This relationship enables us to define a coefficient of friction $\mu$; thus, $F = \mu F_l$. This empirical law was explained by the adhesion model of Bowden and Tabor [1]: If $S$ is the shear strength of the contact points and $A_r$ the real area of contact, the shearing friction is $F = S A_r$. Since the real area of contact is proportional to normal force for both elastic and plastic deformation when multiple asperity contacts are involved, the friction force for macroscopic bodies is generally proportional to normal force.

In the single asperity regime, this functional dependence of $A_r$ on $F_l$ ($A_r \propto F_l$) holds only in case of plastic deformation. Assuming a Hertzian deformation of the contact, the area of contact is $A_r = \pi [K(F_l - F_p)R]^{2/3}$ where $K$ is the elastic modulus, $R$ is the radius of curvature and $F_p$ the pull-off force. Thus, a $2/3$-power law is predicted for the friction: $F = S \pi [K(F_l - F_p)R]^{2/3}$ provided that the shear strength is constant. Hertzian deformation is a rather simple approximation and it applies usually for high loads. The contact area can be estimated more accurately in case of low loads adhesion by DMT or JKRS theory. In particular for JKRS the friction force is:
\[ F \propto S(R/K)^{3/2}[(F_l - F_p) + 2F_p + \sqrt{4F_p(F_l - F_p) + 4F_p^2}]^{2/3}. \]

Thus, one would expect that the friction force microscopy would reveal exclusively non-Amonton like friction behavior. However, although JKRS or extended-JKR type\(^1\) of friction have been indeed observed [2, 3, 4], there are cases [5, 6] where linear dependence is observed. The reason for this rather unexpected finding is believed to be nanometer-scale roughness of the tip (in these studies the sample is believed to be atomically flat, e.g. mica) making it to behave like a multiasperity contact. Thus, “single” asperity contact does not lead automatically to a non-Amonton like friction law.

Unexpected and counterintuitive type of behavior is also encountered on the effect of shear velocity on the friction force. For two macroscopic bodies fluid dynamics implies that the friction force is proportional to the relative velocity \(v\) of the solids (“viscous” friction). In dry\(^2\) contacts the two bodies almost always exhibit static friction and while sliding there is a weak dependence on \(v\). Simulations and perturbation theory has shown that [7, 8] for incommensurate solids no static friction is needed and a viscous low holds. The reasons for these unexpected behaviour for macroscopic solids are speculated to be 1) disorder and impurities that can generate deformation of charge-density waves [9] at large length scales and/or 2) surface roughness that could also produce pinning. Since these reasons are intrinsically macroscopic for microscopic contacts of two solids one expects a viscous law to hold.

In this chapter, we will investigate the effect of applied load and shear velocity on friction force exerted on the SFM tip while scanning a surface filled with pinned-micelles. In addition, we compare the local friction coefficient of the single PS globules with the average coefficient of friction for the pinned-micelle surface. The reason for this investigation is three-fold: 1) based on the analysis above, we expect that these measurements will characterize further the polymer surface layer and 2) since the SFM is still a relatively young technique a demonstration of its capabilities as a surface characterization tool on polymers and on frictional properties is still useful 3) we show that due to local variation in topography three friction coefficients can be defined: \(\mu_0\) (local, excluding roughness); \(\mu_1\) (local, including roughness); \(\mu_{av}\) (average, including roughness). We describe their interconnection.

### 6.2 Experimental Part

#### 6.2.1 Friction Force Images

The friction force images were taken in the usual mode of perpendicular scans (the scanning is performed perpendicular to the long axis of the cantilever beam and the output

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\(^1\)Meyer et al. [2] used in addition to constant shear \(S\) pressure dependent shear \(S = S_0 + aP\). Carpick et al. [3] examined the effect of nonparabolic tips. It has to be noted that the original JKRS equations while hold exactly for parabolic tip profiles and quite accurately for spherical tips, deviate considerably for arbitrary nonparabolic tips.

\(^2\)Meaning no lubricant in the interface.
of the horizontal two quadrants of the photodiode-detector is measured. In this arrangement, as the tip moves on the sample the lateral forces will cause the cantilever to twist. Therefore the light intensity between the left and right detectors will be different. The differential signal between the left and right detector can be related to the degree of twisting, hence to the magnitude of friction force.

### 6.2.2 Quantitative Friction Measurements

The quantitative friction measurements that are presented in this chapter were taken in a different mode called “height” mode with parallel scans [10, 11]. The long axis of the cantilever is parallel to the surface of the sample; otherwise, one has to take into account the tilt angle [11]. The scanning is performed parallel to the long axis of the cantilever (fig. 6.1). In this case the vertical deflection of the cantilever is associated not only with the topography but also with the friction force.

![Figure 6.1: (a,b) Left-to-right scanning of the tip: the piezo withdraws in order to keep the cantilever’s deflection constant; the normal force decreases by \( \Delta F_1 \). (c,d) Right-to-left scanning of the tip: the piezo advances in order to keep the cantilever’s deflection constant; the normal force increases be \( \Delta F_2 \).](image)

We assume that the normal force will be the same \( (F_0) \) when the tip is stationary. The friction force will have the same magnitude \( F \) but opposite direction. The cantilever vertical deflection is set at a constant level, it is the total force (normal force + friction force) exerted to the cantilever that keeps the cantilever at this level. Since the friction force is in opposite directions as the scanning direction is reversed, the normal force has to adjust accordingly to keep the vertical deflection constant. The total moment has to
be the same at both scanning directions. Hence, if we take the reference point to be the point where the cantilever joins the holder, we have:

\[(F_0 - \Delta F_1)L + F\alpha = (F_0 + \Delta F_1)L - F\alpha\]  \hspace{1cm} (6.1)

where \(L\) is the long axis of the cantilever and \(\alpha\) is the vertical distance between the end of the tip and the base of the cantilever. Thus

\[F = \frac{(\Delta F_1 + \Delta F_2)L}{2\alpha}\]  \hspace{1cm} (6.2)

The coefficient of friction \(\mu\) between the tip and the sample is then given as

\[\mu = \frac{(\Delta F_1 + \Delta F_2)L}{2F_0\alpha}\]  \hspace{1cm} (6.3)

The absolute difference of the normal force \(\Delta F_1 + \Delta F_2\) between the two scans (forward and reverse) can be measured directly by the the height difference of the piezo between the two scanning directions multiplying it with the spring constant \(k\). The normal force \(F_0\) is also \(F_0 = kZ_0\) where \(Z_0\) is the initial cantilever deflection. Thus

\[\mu = \frac{\Delta Z L}{Z_0 2\alpha}\]  \hspace{1cm} (6.4)

If one measures the height difference \(\Delta Z\) at different normal loads \(F_0\) the effect of the adhesion is also taken into account as a set off force. In fact, this is another way to measure adhesion, since extrapolation of the curve towards negative normal forces will intercept the normal force axis at the adhesion-force value.

As one can see in the above equation 1) the friction coefficient depends only on geometric parameters of the cantilever and not on the normal spring constant (as, perhaps, one would expect) 2) in addition and most importantly, it is not necessary to solve the (non-trivial) material problem of cantilever torsion in order to determine its lateral spring constant.

It is important to note that this equation is derived under the assumption that the friction force \(F\) is the same for both forward and reverse scanning. This is an approximation since the normal force is slightly different for the two opposite scans. However, this difference is expected to be much smaller than \(F_0\) and the correction is of a higher order.

For the measurements reported here the height differences were measured directly from “parallel” forward and reverse linescans: \(\Delta Z = (\text{average height of reverse profile}) - (\text{average height of forward profile})\).
6.3 Results and Discussion

6.3.1 Frictional Properties of the Grafted Monolayers

In fig. 6.2b a typical lateral force image of a gold substrate full of pinned PS micelles simultaneously taken with the topography image in fig. 6.2a (PS$_{500}$-SH). All the examined polymer monolayers gave similar friction images. We see (as with the single isolated polymer globules) the resemblance between the slope of surface topography and the corresponding friction.

Variation of the friction forces with the normal load is presented in fig. 6.3a (measurements were taken as described in subsection 6.2.2). We observe a linear increase of the friction forces for the range of the applied loads used ($\approx$ 1 to 10 nN). This can be explained by the fact that neither the tip nor the polymer sample are smooth enough. For example the profiles of fig. 4.7 reveal that the pinned micelle surface could be quite rough in the nanometer–subnanometer scale. Although, the tip-sample contact is elastic its friction behavior is Amonton-like due to the corrugation that produces polyasperity contact. The coefficient of friction was calculated to be 0.45 which compares favourably with the coefficient of friction of bulk polystyrene, 0.515 [13]. Linear extrapolation of the loading curves shows small but consistent negative interception with the horizontal axis that is associated with the presence of adhesive forces. Adhesion force estimated from this extrapolation is close to the pull-off force measured from force-distance curves: around 2 nN.

Results of friction forces as a function of sliding velocity is shown in fig. 6.3b (produced as it is described in subsection 6.2.2). We observe linear increasing friction for the range of the velocities used (4 to 200 $\mu$m/s). This is the expected behavior for solids$^3$. The

$^3$Glosli and McClelland[12] showed that for ordered organic monolayers the effect is associated with growing dissipation of accumulated energy at higher shear velocities.
sliding velocity dependence shows that polymer globules of a few PS chains are in the usual glassy state (glass transition temperature for PS is around 100°C).

No hysteresis behavior or signs of wear were observed even after hundreds of sliding cycles. These findings indicate that the grafted polymer monolayer is robust and stable, and display only elastic deformation under the shear forces that we have applied.

Figure 6.3: Height difference between forward and reverse scanning (which is proportional to the friction force) as a function of the external load (a) and the sliding velocity (b).
6.3.2 Relationship between the Local Friction Coefficient and the Average Friction Coefficient

In chapter 5, we measured the local friction coefficient on single PS$_{1400}$-SH globules to be 0.3 by the “zero-torsion” method. The same value was obtained for the local friction coefficient of the PS-SH pinned micelles$^4$. However, The “average” friction coefficient was measured to be 0.45 for the PS$_{500}$-SH. We will try now to explain this difference. Ploughing is excluded since we noticed no damage on the sample. We employ the ratchet mechanism of friction$^{[14, 15]}$. The force balance for a tip sliding over an asperity is considered in fig. 6.4. The load $F_l$ (normal to the general surface is constant. The friction force$^5 F$, would be constant and equal to $\mu_0 F_l$ if the surface was smooth; but this is not the case. the friction force varies as a function of the surface roughness. If we analyze the forces $F$ and $F_l$ to two components $F_t$ and $F_n$ tangential and normal, respectively, to the local surface of the sample at the contact point we have

$$F_n = F_l \cos \theta + F \sin \theta$$  \hspace{1cm} (6.5)

$$F_t = F \cos \theta - F_l \sin \theta$$  \hspace{1cm} (6.6)

Where $\theta$ is the angle of the asperity’s tangent at the contact point with the horizontal plane.

Figure 6.4: Schematic drawing showing the effect of roughness on the friction forces in SFM measurements. $F_l$ is the externally applied load, $F$ the friction force with respect to the general surface, $F_t$ and $F_n$ are the force components along and perpendicular to the surface of the contact that coincides with the local surface of the sample (for not severe deformations). $\theta$ is the local angle of the asperity with respect to the horizontal plane.

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$^4$The measurement is difficult for the smaller molecular weights because of the small size of the pinned micelles and the convolution effect.

$^5$We call now friction force the total lateral force exerted on the tip.
The local coefficient of friction (without the roughness effect) is

$$\mu_0 = \frac{F_t}{F_n}$$  \hspace{1cm} (6.7)

The local coefficient of friction including roughness is given by

$$\mu_1 = \frac{F}{F_t} = \frac{\mu_0 + \tan \theta}{1 - \mu_0 \tan \theta}$$  \hspace{1cm} (6.8)

Usually $\mu_0 \tan \theta$ is small, and since $\tan \theta = \frac{dz}{dx}$ (slope of topography), we obtain

$$\mu_1 \approx \mu_0 + \frac{dz}{dx}$$  \hspace{1cm} (6.9)

indicating that indeed the friction signal changes as the slope of the topography.

For a symmetrical asperity with constant slope the average coefficient of friction that the SFM tip experiences while scanning across the whole asperity is

$$\mu_{av} \approx \mu_0 (1 + \tan^2 \theta)$$  \hspace{1cm} (6.10)

if $\mu_0 \tan \theta \ll 1$; $\theta$ now is an average over the whole surface. We emphasize that this is the friction coefficient that one measures comparing forward and reverse SFM scannings and this friction coefficient is to be compared with macroscopic measurements.

For the $\text{PS}_{500}$-$\text{SH}$ pinned-micelles the $\theta_0$ follows simply by the triangle in fig. 6.5 to be

$$\theta_0 = \sin^{-1} \frac{w_p}{R_t + r}.$$  

For $w_p = 17 \text{ nm}, R_t = 50 \text{ nm}$ and $r = 11 \text{ nm}$ we obtain that $\theta_0 \approx 16^\circ$. Hence, $\theta_{av} \approx 8^\circ$. Thus $\mu_{av} \approx \mu_0 + 0.02$. We can calculate $\mu_{av}$ using the pinned-micelles

approximate shape (spherical cap) and dimensions (see chapter 3), without using the approximation $\mu_0 \tan \theta \ll 1$. Since only the upper part of the polymeric spherical caps is probed the calculation involves the integral

6however, it certainly includes the atomic scale “roughness” (atomic corrugation)
\[ \mu_{av} = \frac{1}{2\theta_0} \int_{-\theta_0}^{\theta_0} \frac{\mu_0 + \tan \theta}{1 - \mu_0 \tan \theta} d\theta = \frac{1}{2\theta_0} \ln \left( \frac{1 + \mu_0 \tan \theta_0}{1 - \mu_0 \tan \theta_0} \right) \]  \hspace{1cm} (6.11)

where the angles are measured in rad. Substituting \( \theta_0 \approx 16^\circ = 0.279 \) (rad), we obtain \( \mu_{av} = 0.309 \). It is clear that, although the corrugation can explain the observed contrast, it cannot account for the measured value of the average friction coefficient.

The most possible explanation is adhesive force and contact area differences induced by the variations in topography: In fig. 6.6 we show schematically the tip (large circle) in position a (between two pinned micelles) and in position b (on a pinned micelle). In position a, the contact area between the tip and sample is bigger than in position b for two reasons: 1) the adhesive interaction is larger in the valley since it is closer to the average sample surface (for example for van der Waals forces and a sphere-plane system: \( F_{vdw} \propto 1/D^2 \), where \( D \) is the separation); 2) due to the local geometry of the sample (valley). As the tip scans the pinned-micelle surface, it moves successively from positions like a to positions like b (valley \( \rightarrow \) peak \( \rightarrow \) valley \( \rightarrow \) ...). This process is expected to involve spontaneous jumps and hysteresis\(^7\), therefore to be irreversible and to dissipate energy\(^8\). This is an extra dissipation mechanism that is not included in \( \mu_0 \). As we have mentioned this friction coefficient applies for a smooth surface, where it is expected that there is no large adhesion and contact surface variation. One could argue that the feedback loop compensates for the effect; However, the feedback does not operate ideally and it applies only vertically.

\[ \begin{array}{c}
\text{Figure 6.6:} \ a. \ The \ tip \ is \ situated \ between \ two \ pinned-micelles. \ b. \ The \ tip \ is \ on \ a \ top \ of \ a \ globule. \end{array} \]

\(^7\)It compares with forward-reverse force distance curves. Simple examples of “bonding-debonding cycles” are described in ref. [16].

\(^8\)Semiqualitative treatment of the correlation between friction and “adhesion hysteresis” is given by Israelachvili [17].
6.4 Conclusions

Investigating the frictional properties of the pinned-micelle monolayers we found 1) that the monolayer exhibits solid-like frictional properties; 2) the average friction coefficient compares well with the friction coefficient for bulk polystyrene; 3) Comparing the average friction coefficient of pinned-micelle monolayers ($\mu_{av}$) with the local friction coefficient on a polystyrene globule ($\mu_0$) we observed a 33% difference, with the $\mu_{av}$ being the larger. We showed that a model incorporating solely the surface roughness is not adequate to account for this increase. We argue that the discrepancy is due to differences in adhesive force and contact area induced by the corrugation.

References


