Sliding friction
*From microscopic contacts to Amontons’ law*

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4.1 Abstract

In this chapter we show how the area of contact between two objects can be detected by using the strong enhancement of the fluorescence of rigidochromic probe molecules attached to one of the surfaces. Confinement of the molecules suppresses nonradiative decay and turns on the fluorescence. The approach is demonstrated by imaging of the contact area of plastic, glass and teflon spheres in contact with a flat glass surface. Our results agree excellently with the prediction of Hertz’ classical theory based on elastic deformation.

4.2 Introduction

The study of contact mechanics dates back to 1882 with the publication of “On the contact of elastic solids” by Hertz[2]. For the behavior of virtually all mechanical systems, the mechanics of the contact between their constituents is crucial. Friction, for instance, is a direct consequence of contact mechanics and is responsible for about 30% of the world energy consumption[3]. Surprisingly little is known about how friction emerges from the physical contact between objects[4, 5]; the main challenge is that since most (if not all) surfaces possess a certain roughness, the actual contacts may occur on
microscopic length scales, even for large macroscopic bodies. Bowden and Tabor were the first to emphasize the importance of surface roughness for bodies in contact[6].

In this chapter we describe the first direct visualization of mechanical contacts at the microscale by means of fluorescence microscopy, using specifically developed probe molecules that fluoresce when confined in a contact. To achieve this goal we synthesized rigidochromic fluorescent molecules that fluoresce only very weakly in (low-viscosity) solutions owing to the presence of rapid non-radiative relaxation pathways for the excited state[7, 8, 9]. This fast non-radiative decay is triggered by the rotation around a specific bond in the molecule[10]. When the rotation of the bond is hindered, the non-radiative decay is suppressed, and the excited state decays by emitting a photon. When rigidochromic molecules are incorporated in a very viscous medium, such as a glassy polymer matrix, a strong fluorescence is observed. This effect has been used to measure local viscosities in polymer films and study their free volume and glass transition[11, 12, 13, 14], and to investigate the viscosity of membranes and intracellular media[15, 16, 17]. We show that the confinement between two surfaces also impedes the non-radiative relaxation of the probe molecule 1 (Figure 4.1) that starts fluorescing strongly when confined. This effect then allows the detection of the physical contacts between surfaces on a molecular scale.

4.3 Experiment

For our experiments, we synthesized a new member of the DCDHF class of compounds that has in recent years been developed by Moerner, Twieg, and co-workers for single-molecule imaging[15, 17, 18] (Figure 4.1). This chromophore has advantages over previously used viscosity sensitive probes such as dicyanovinyljulolidines[7, 8, 19] and BODIPY dyes[20, 21]: excitation and emission in the visible part of the spectrum, good photostability[15], and particularly low fluorescence in low-viscosity polar solvents. Compound 1 was chemically linked to the surfaces of glass coverslips to investigate the imaging of contact areas. Compound 2 was used for comparison.

As a first step to characterize their photophysical properties, we measured absorption and emission spectra of compounds 1 and 2 in a series of solvents (Appendix A); there is little difference in the properties of 1 and 2, as expected. Both show a weak solvatochromic effect in absorption and in emission. The fluorescence quantum yields $\Phi_f$ are low, and tend to decrease with increasing
4.3 Experiment

Figure 4.1: The compounds investigated in this study. The $\beta$ and $\gamma$ bond can twist to facilitate excited state deactivation[10].

solvent polarity. Fluorescence decay times $\tau_f$ follow the same trends as the quantum yields. In some solvents they were shorter than the time resolution of our instrument ($< 10$ ps). The quantum yields and decay times are larger in solvents of higher viscosity. For example, in cyclohexanol $\tau_f = 0.46$ ns, and $\Phi_f = 0.11$, while in 2-propanol $\tau_f = 0.040$ ns and $\Phi_f = 0.010$ (see Appendix A). The reason for the difference is that in low-viscosity solvents rapid nonradiative deactivation of the excited states occurs by twisting of the exocyclic $C = C(CN)_2$ bond, as was reported previously for DCDHF chromophores[15]. In some solvents we found a bi-exponential fluorescence decay, indicating that the photophysical behavior of this chromophore is more complicated[10] than was suggested previously[11, 15].

We systematically studied the effect of solvent viscosity with minimal effect of polarity by subjecting solutions of compound 1 in acetonitrile to different hydrostatic pressures. To convert the hydrostatic pressures to changes in viscosity, we used the relationship between viscosity of acetonitrile and pressure described by Martin et al.[22] using data from Dymond et al.[23]. The results are shown in Figure 4.2. We find that the fluorescence intensity can be described well by the Förster-Hoffmann equation[24]:

$$\log(I_f) = A \cdot \log(\eta) + C$$

(4.1)

In Equation 4.1, $A$ is a constant that depends on the dye and the solvent[19]. From the slope of the line shown in Figure 4.2b we find $A = 0.66 \pm 0.04$. For other systems with the same type of rotor unit, values of $A$ between 0.5 and 1.2 were recently reported, depending on the nature of the solvent[19].
To be able to look at the contact of an object with a flat surface, we covalently attached probe 1 to glass cover slips. The latter were functionalized with N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane and the dye was attached using an amide bond. Fluorescence emission and excitation spectra of surfacebound 1 were found to be very similar to those of 1 and 2 in solution. The absence of broadening of the bands shows that aggregation of surfacebound dye molecules does not occur or has no significant effect on the electronic structure of the chromophore.

On the other hand, the fluorescence lifetime of the bound molecules is quite different. The fluorescence decay was measured at several locations on air-dried cover slips using the single photon timing unit of a confocal microscope. The time profiles were fitted using a double exponential function. A slow decay component ($\tau_1 = 1.4 \pm 0.2$ ns) was found to be present in addition to a faster one ($\tau_2 = 0.36 \pm 0.04$ ns). The average lifetime, for each point, amounted to $\tau_{av} = 0.7 \pm 0.2$ ns. The deviation from single exponential decay can be attributed to spatial heterogeneity: the surfacebound probe may exist in different local environments, in which the molecules have different nonradiative decay rates.

The quantitative measurement of fluorescence intensities of dye monolayers is difficult owing to the very weak absorption. Therefore we use the
average lifetime to quantify the fluorescence intensity of the dye on the cover slip[25, 26]. The quantum yield is expected to be linearly dependent on the lifetime as \( \Phi_f = \tau_{av} \cdot k_f \), where \( k_f \) is the radiative decay rate constant of the chromophore. The values of \( \Phi_f \) and \( \tau_{av} \) for compound 1 in several solvents give \( k_f = 0.24 \pm 0.06 \text{ ns}^{-1} \). We do not observe a systematic dependence of \( k_f \) on solvent polarity, and we assume that it does not change significantly when the dye is bound to the surface. Then, based on \( \tau_{av} = 0.7 \text{ ns} \) for cover slips functionalized with rigidochromic probe 1, we can estimate the fluorescence quantum yield to be about 0.17. Thus, on the cover slip, the emission of the probe is considerably stronger than in solution, but weaker than reported for 2 in the poly(methyl methacrylate) (PMMA) matrix. This is because the surface-bound probe molecules interact strongly with the surface, reducing the freedom of intramolecular rotation.

To obtain a suitable dynamic range for the rigidochromic effect, we immersed the slides in DMSO. This led to a clearly weaker emission, because the chromophore is solvated and free to undergo rotational motion in the excited state. The lifetime is reduced to \( \tau_{av} = 0.31 \pm 0.02 \text{ ns} \), corresponding to a fluorescence quantum yield of about 0.07. Thus, although the fluorescence is still stronger than in the solution, the nonradiative decay is faster than on the air-dried cover slips. We generated contacts of PMMA spheres pressed onto the probe-functionalized cover slip, immersed with DMSO. A force transducer was used that exerts and records a well-defined force. Fluorescence was excited and detected through the cover slip, using an epifluorescence confocal microscope. The DMSO serves a dual purpose in these experiments: it not only reduces the fluorescence intensity before the contact is established but also provides a sufficient matching of the refractive indices of the glass and PMMA to avoid the effects of refraction of light at the interfaces.

### 4.4 Results

When the sphere is pressed onto the cover slip, the confinement leads to a clear fluorescence increase owing to the rigidochromic effect: a roughly circular fluorescent spot appears and increases in size as the force is increased (Figure 4.3). When the sphere is retracted and placed again with the same load, the contact area is reproduced within \( \pm 5\% \).

In Hertz’ classical theory[2], which was exactly devised for this situation, the radius \( a \) of the contact area between a sphere (radius \( R \)) and a flat surface pressed against each other with force \( N \) is described by:
Figure 4.3: Representative fluorescence intensity images with the focal plane positioned at the surface of a cover slip with covalently linked dye 1. A 4 mm PMMA sphere is pressed on the cover slip with the indicated loads, resulting in an increase in the contact area in which the fluorescent probe lights up. The red circles indicate the Hertzian sphere-on-flat contact area defined by Equation 4.2 using $E^* = 1.92$ GPa and $R = 2$ mm. The size of the images is $160 \mu m \times 160 \mu m$.

In Equation 4.2, $E^*$ is the plain strain elastic modulus of PMMA; the modulus of glass can be ignored because it is more than 30 times higher
than that of PMMA. We measure the PMMA modulus by recording the relation between deformation and force when a PMMA sphere is squeezed between two plates by a tensile tester (see chapter 2 for details) and find $E^* = 1.92 \pm 0.1$ GPa. We plot the contact circles predicted by Hertz theory using $E^* = 1.92$ GPa and $R = 2$ mm onto the experimental contacts in Figure 4.3. Hertz theory, without adjustable parameters, agrees remarkably well with the experiments, which strongly supports the validity of using immobilized compound 1 as a probe for mechanical contact. In Figures 4.4, 4.5 and 4.6 we demonstrate that the technique also works for different sphere materials.

We note that in all experiments the fluorescent spot is not perfectly circular, and shows a significant amount of structure within it, implying that there are many small contacts at the microscopic scale, rather than one large homogeneous contact, as is assumed in Hertz theory. The deviation from full circular contact is caused by the surface roughness of the sphere; micrometric valleys and scratches on the sphere surface are visible as gaps in the contact area. These roughness features however become less important at higher contact forces where the radius of the contact area becomes much larger than the typical roughness length scale. In Figure 4.7 we show the relation between normal force and real contact area, defined as the area within which the probe lights up (see also chapter 2). The next chapters will describe the real contact area and its importance in friction in more detail.

## 4.5 Conclusion

In summary, the present approach offers a unique method to directly observe the detailed structure of the contact area between two surfaces. We obtain diffraction-limited resolution in the imaging plane, but the resolution in the axial direction is determined by the thickness of the monolayer of dye molecules on the flat glass surface (roughness < 1 nm).
Figure 4.4: Fluorescence intensity images with the focal plane positioned at the surface of a cover slip with covalently linked dye 1. A 560 µm polystyrene (PS) sphere is pressed on the cover slip with the indicated loads, resulting in an increase in the contact area in which the fluorescent probe lights up. The red circles indicate the Hertzian sphere-on-flat contact area defined by Equation 4.2 using $E^* = 3.7 \text{ GPa}$ and $R = 280 \mu\text{m}$. The PS elastic modulus was measured using a tensile tester (chapter 2). The size of the images is 80 µm × 80 µm.
Figure 4.5: Fluorescence intensity images with the focal plane positioned at the surface of a cover slip with covalently linked dye 1. A 4 mm glass sphere is pressed on the cover slip with the indicated loads, resulting in an increase in the contact area in which the fluorescent probe lights up. The red circles indicate the Hertzian sphere-on-flat contact area defined by Equation 4.2 using $E^* = 25$ GPa and $R = 2$ mm. The size of the images is $90 \mu m \times 90 \mu m$. 

Figure 4.6: Fluorescence intensity images with the focal plane positioned at the surface of a cover slip with covalently linked dye 1. A 3.1 mm polytetrafluoroethylene (PTFE) sphere is pressed on the cover slip with the indicated loads, resulting in an increase in the contact area in which the fluorescent probe lights up. The red circles indicate the Hertzian sphere-on-flat contact area defined by Equation 4.2 using $E^* = 0.53$ GPa and $R = 1.6$ mm. The PTFE elastic modulus was measured using a tensile tester (chapter 2). The roughness of the PTFE sphere is large compared to the size of the Hertzian contact area. The size of the images is $360 \mu m \times 360 \mu m$. 
Figure 4.7: The real contact area for all four materials. To extract the real contact area from the images we use the method described in chapter 2. The contact pressures are roughly 23 MPa for PTFE, 60 MPa for PMMA, 164 MPa for borosilicate glass and 318 MPa for PS.
4. FLUORESCENCE MICROSCOPY VISUALIZATION OF CONTACTS BETWEEN OBJECTS
Bibliography


