Development of an atomic force microscope closed fluid cell for tribological investigations of large samples in chemically aggressive environments

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Abstract: Many atomic force microscopes (AFM) are nowadays equipped with closed fluid cells. Most of these closed fluid cells have small volume, limiting the maximum sample size, and, furthermore, do not allow for investigations in chemically aggressive environments such as solvents. The closed fluid cell for MFP-3D, the atomic force microscope from Asylum Research, Santa Barbara, CA, has a glass base and is mainly intended for investigations of flat transparent biological samples.

Starting from the MFP-3D closed fluid cell, a fluid cell tailored for investigations in tribologically relevant environments, e.g. at extreme mechanical and chemical conditions which may vary with time, was developed. Samples of various shapes and sizes can thus be investigated in controlled environments, be they fluid (e.g. solvents) or gaseous (e.g. corrosive gases).

First results of AFM nanotribology experiments using this fluid cell are presented. Among the systems of interest are additives diluted in solvents adsorbing to surfaces and spreading and persistence of ionic liquids on tribologically stressed surfaces.

Keywords: atomic force microscopy in solvents, atomic force microscopy closed fluid cell, chemically aggressive conditions, nanotribology

1 INTRODUCTION

Atomic force microscopy (AFM) is a scanning probe microscopy technique that is widely used in nanotribology. For basic papers on AFM, see references [**1**] to [**5**], and for application of scanning probe microscopy techniques in various fields see references [**6**] to [**10**]. A good overview on ambient and UHV AFMs and their specifications is given in reference [**11**]. Novel high-speed AFM (performed at video rates) shall open completely new possibilities for tribological investigations on the single molecule level in real time [**12**].

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Many atomic force microscopes are nowadays equipped with closed fluid cells. Most of these closed fluid cells have small sample volumes: they are designed for biological samples that need a very precise control of environmental parameters, such as temperature, pH value, and the like.

Closed fluid cells currently available allow for sample volumes in the range of 50 μl to about 1 ml. While perfect for many biological applications, the small maximum sample volume of such conventional closed fluid cells severely limits the maximum sample size. Furthermore, the design of the conventional closed fluid cells does not allow for investigations in chemically aggressive environments such as solvents or corrosive gases. Therefore, most of the conventional AFM closed fluid cells are unsuitable for most tribological studies.

Tribological samples often need to be quite large (up to a few centimetres in length or diameter), so that macroscopic wear and friction experiments are possible in addition to nanotribological studies on the same area without sample alteration due to cutting, cleaving, polishing, dismantling, and the like [**13**]. Also, measurements at extreme chemical conditions are essential, e.g. in solvents or corrosive fluids.

Responding to these needs, a modified AFM closed fluid cell for tribological investigations of large samples in chemically aggressive environments was designed and constructed.

2 MATERIALS AND METHODS

CCELL, the unmodified closed fluid cell provided with the AFM (MFP-3D, Asylum Research, Santa Barbara, CA, USA), allows for investigations of flat samples in controlled environments (see Fig. 1 for the lower part of the fluid cell). In the closed configuration, the fluid cell is sealed at both the top and bottom.

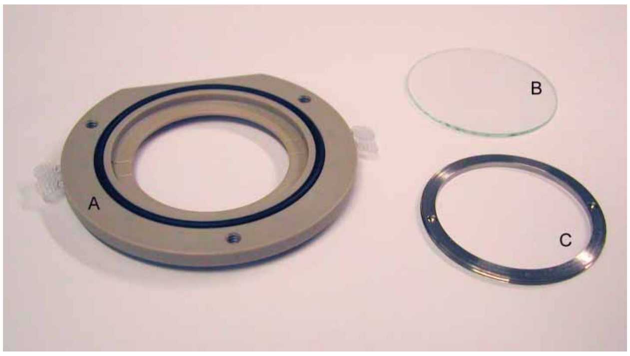


Fig. 1 Lower part of the conventional closed fluid cell supplied with the MFP-3D. (A) Base with plugged Luer fittings, (B) glass disc sample holder, and (C) ring for fixing the glass to the base

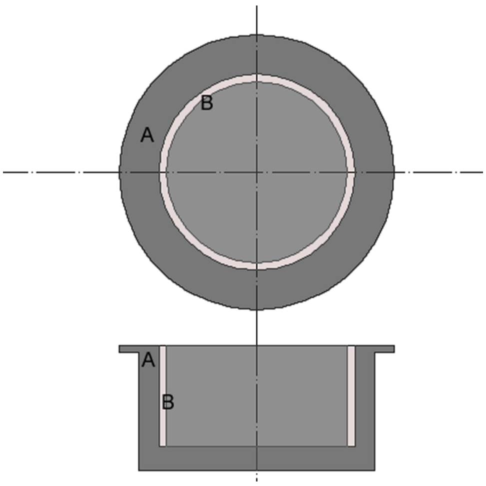


Fig. 2 Container pot of the modified AFM closed fluid cell for tribological investigations of large samples in chemically aggressive environments, top and side view

Four fluid exchange ports (Luer fittings, Fig. 1(A)) allow for exchange and monitoring of sample environment during the measurements (gas or fluid exchange; insertion of sensors for e.g. temperature, pressure, or humidity). Furthermore, electrochemical experiments as well as measurements in chemically aggressive solvents are possible. The possible pH range is between 1 and 14.

The maximum sample volume in the unmodified fluid cell is ~1 ml and the maximum sample height is 2 mm.

In many cases relevant for tribological investigations, samples have larger volume and are not flat. To minimize sample preparation (and thereby possible sample alteration), a modified AFM closed fluid cell (Figs 2 to 5) for tribological investigations of large

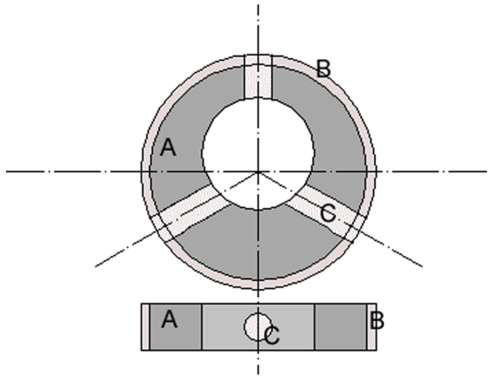


Fig. 3 Sample holder for the modified AFM closed fluid cell for tribological investigations of large samples in chemically aggressive environments, top and side view

Fig. 4 Modified AFM closed fluid cell for tribological investigations of large samples in chemically aggressive environments. (A) Stiff spring, (B) spanner, (C), (D), and (E) container pots, and (F) sample holder

Fig. 5 Assembled modified AFM closed fluid cell for tribological investigations of large samples in chemically aggressive environments. The sample is an M4 brass screw nut, 1 cm in diameter, 5 mm high

samples in chemically aggressive environments starting from the CCELL was constructed, built, and tested. This new fluid cell is ideally suited for the requirements described above while maintaining most advantages and the compatibility of the original fluid cell.

Requirements for the modified fluid cell comprise:

(a) high durability regarding resistance to the chemical properties of the contained fluid;
(b) ability to contain and fix samples up to a few centimetres in size;
(c) possibility for further extensions in volume and function;
(d) easy to dismantle and clean.

The 35 mm diameter glass disc sample holder of the original fluid cell is replaced by a cylindric container pot with an internal fine thread (M25 × 1.5) made from stainless steel (Fig. 2). The stainless steel sample holder base (Fig. 3) is fitted into the container pot screwing the external fine thread of the holder into the internal fine thread of the container pot (B in Fig. 2). The sample is fixed by one or several grub screws (slugs) to the sample holder, which in turn fits into the container pot.

The stiff spring (Fig. 4(A)) is inserted at the bottom of the respective container pot (Figs 4(C) to (E)) and presses against the sample holder (Fig. 4(F)), preventing play in the fine thread. The sample holder (Fig. 4(F)) height in the respective container pot (Figs 4(C) to (E)) is adjustable along the fine thread with an appropriate spanner (Fig. 4(B)). The spanner (Fig. 4(B)) is also used to tighten the ring (Fig. 1(C)) for fixing the container pots to the base.

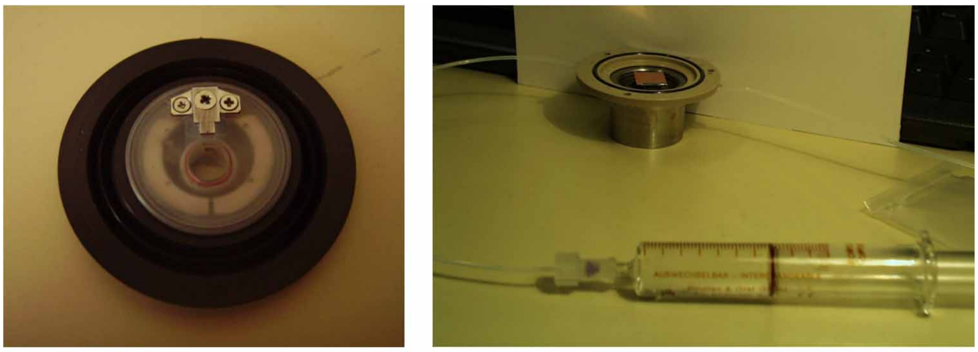
The stainless steel parts of the modified fluid cell were machined in the workshop of the Institut für Allgemeine Physik at Vienna University of Technology. Three different sizes of container pots were fabricated, thereby permitting the modified fluid cell to firmly hold samples of various shapes and sizes (Figs 4(C) to (E)). The assembled modified fluid cell with a sample (M4 brass screw nut) is shown in Fig. 5.

The modified closed fluid cell holds a maximum of 3.5, 6, and 8.5 ml of liquid, depending on which container pot is used. The maximum possible sample height is 2.2 cm and the maximum possible sample diameter is 1.2 cm.

Replacing the stainless steel pots with aluminium pots is possible. This reduces the mass of the set-up, but also reduces resistance to chlorinated/halogenated solvents.

For the measurements in closed configuration, there is a special mounting technique to be followed. The fluid cell is assembled according to the provided instruction, so that two channels on opposite sides of the fluid cell are closed. Instead of the sapphire glass, the aluminium part is mounted.

After screwing together the upper and lower parts of the fluid cell (Fig. 6), it is filled with the desired fluid (e.g. heptan, as described below) and mounted on the AFM head.



(a) (b)

Fig. 6 (a) Upper half of the fluid cell, with the black Viton^{TM} membrane; and (b) lower half of the fluid cell with the new aluminium part and a syringe with solvent attached to the Luer fittings

Fig. 7 Assembled measurement system – syringe filled with solvent plus additive solution

The AFM head is then mounted on the moving table (Fig. 7) and the height is adjusted, so that the whole fluid cell lies on the moving table.

When the mounting procedure is completed, preliminary friction measurements in the pure solvent can be started. After recording the friction signal in pure solvent, additives dissolved in the solvent can be introduced into the system (see Fig. 7) and friction measurements in the additive solution can be started.

After finishing the measurements, the fluid cell is demounted, disassembled, and cleaned.

3 RESULTS AND DISCUSSION

The modified fluid cell fulfils all requirements concerning durability, sample volume, expandability, and taking apart for cleaning as introduced above.

An overview of the experiments performed and the results obtained are given in Tables 1 and 2.

First exploratory measurements using the extended fluid cell were performed with AFM contact mode on 100 Cr6 steel roller bearing parts in toluene in the open-cell configuration (Table 1, Figs 8 to 10). The investigated 100 Cr6 steel part has a diameter of 10 mm and a height of 14 mm. The depth of the wear marks is ∼300 nm. In Figs 8 and 9 the image sizes are $30\times30\,\mu m^2$ and $2\times2\,\mu m^2$, respectively. The scan rate in both images is 0.5 Hz, with an integral gain of 15. The cantilevers used are standard Olympus Si cantilevers with a spring constant of 2 N/m and a resonant frequency in air of 59 kHz.

AFM contact mode imaging of wear scars on a 100 Cr6 steel cylinder from a roller bearing in toluene proved to be entirely trouble-free (see Figs 8 and 9). The top-view optics of the MFP-3D allow for visual inspection of the sample with optical microscopy while approaching the cantilever. This is very important especially for rougher tribologically interesting samples, since too rough sample areas can successfully be avoided. The lateral force signal shows low noise, allowing for friction experiments on the nanometre scale.

AFM intermittent contact mode imaging in toluene tended to be very sensitive to changes in integral gain. In the MFP-3D, the x–y motion of the scan is performed from the sample, not from the tip. Since the container pots are relatively heavy, too fast scanning is not possible because of inertial forces. Using low integral gain (5) and slow scanning (0.5 Hz) lead to

Table 1 Measurements on 100 Cr6 steel roller bearing part with wear marks in pure toluene

Method	Image size	Result
AFM contact mode	$30\times30\,\mu m^2$	Topography ☑
AFM contact mode	$2\times2\,\mu m^2$	Topography ☑
AFM intermittent contact mode	$50\times50\,\mu m^2$	Topography ☑

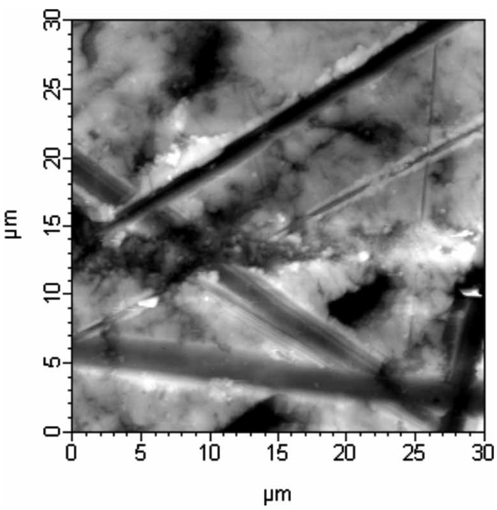


Fig. 8 AFM contact mode image in toluene of wear marks on 100 Cr6 steel in the open-cell configuration. Image size $30\times30\,\mu m^2$

Table 2 Measurements on Cu sputtered silicon wafers in solvent with stepwise increasing ZDDP additive concentrations

Method	Solvent	Result
In situ AFM contact mode, image size: $5\times5\,\mu m^2$	Pure heptan	Topography ☑ friction ☑
	Heptan plus 50.000 ppm ZDDP	Topography ☑ friction ☒
	Heptan plus 200.000 ppm ZDDP	Topography ☑ friction ☑

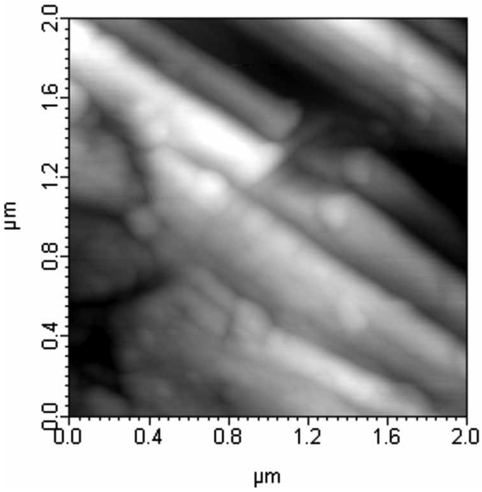


Fig. 9 AFM contact mode image in toluene of wear marks on 100 Cr6 steel in the open-cell configuration. Image size 2×2 μm^2

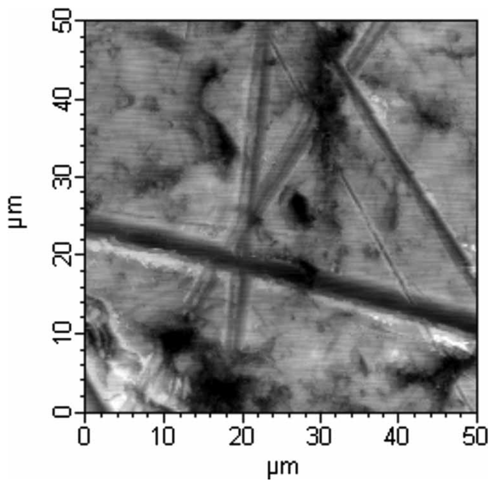


Fig. 10 AFM intermittent contact mode image in toluene of wear marks on 100 Cr6 steel in the open-cell configuration. Image size 50×50 μm^2

clear images (see Fig. 10). The cantilever is a standard Olympus Si cantilever with a spring constant of 2 N/m and a resonant frequency in air of 59 kHz.

Additionally, friction measurements have been performed on the silicon wafers sputtered with copper in closed configuration of the fluid cell (Table 2). Following the calculation technique presented in reference [**14**], ten measurement lines are picked and the friction is calculated. The results are statistically relevant: the error is about half the difference between the largest and smallest friction value.

First, measurements were performed in pure heptan. The friction values of two successive scans in pure heptan were 1.1625 ± 0.15 mV and 1.12075 ± 0.15 mV.

Then, a heptan plus 50.000 ppm ZDDP additive solution (lubrizol, containing 14.7 per cent sulphur, 6 per cent phosphor and 8.1 per cent zinc) was introduced into the fluid cell. However, the obtained results were within the error bars of the control: the friction value of two succesive scans was 1.08 ± 0.15 mV and 1.1175 ± 0.15 mV.

Therefore, in the next step, a higher concentration of the additive was used (heptan plus 200.000 ppm ZDDP additive). The control experiment in pure solvent gave, in two successive scans, friction values of 1.1825 ± 0.15 mV and 1.1515 ± 0.15 mV. When the additives were introduced into the fluid cell, the friction decreased significantly: in two successive scans the friction values were 0.5575 ± 0.15 mV and 0.733 ± 0.15 mV.

The distortions in the picture can be observed while introducing a heptan + ZDDP solution into the closed fluid cell (Fig. 11). The time needed for the AFM tip to retrieve stable measurement conditions again scales with the velocity of fluid introduction.

The modified closed fluid cell holds a maximum of 3.5, 6, and 8.5 ml of liquid, depending on which container pot is used. Such large volumes allow for the use of larger, tribologically more relevant samples. Commercially available closed fluid cells generally have smaller volumes. The closed fluid cell from JPK Instruments (Berlin, Germany) offers a standard version of a closed fluid cell with a volume <150 μl and a small volume version with a volume <70 μl. The closed fluid cell of Asylum Research (Santa Barbara, CA, USA) has a sample volume of 1–2 ml and the volume of the closed fluid cell for the Veeco AFMs is between 50 and 200 μl.

The chemical compatibility of the CCELL is excellent. Measurements are possible in most solvents, and in buffer solutions, alcohols, and ionic fluids [**15**]. Materials that come into contact with the fluid sample environment are fused quartz (SiO_2, from the

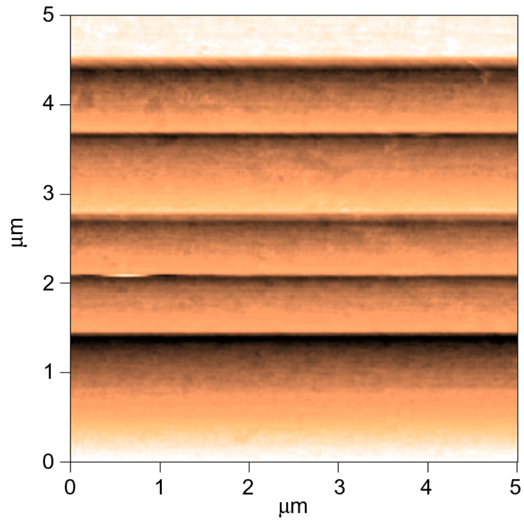


Fig. 11 *In situ* AFM scan. The stripes appear when the heptan + ZDDP solution is introduced into the fluid cell, because the tip intermittently loses connection with the sample

cantilever holder), Kel-F® PCTFE (PolyChloroTriFluoroEthylene) (from the cantilever holder), Viton™ (the large flexible membrane comprising the cover of the upper part of the CCELL, and the O-rings), the stainless steel metal clip that holds the cantilever, the cantilever itself (silicon, silicon nitride), and PEEK™ plastic (the material of the base into which the container pots are inserted).

Kel-F has excellent chemical resistivity. Only tetrahydrofuran and a few halogenated solvents will react with it. This resilient polymer is excellent for fittings and sealing surfaces.

PEEK™ polymer has excellent chemical resistance to organic and inorganic liquids. Concentrated sulphuric acid and concentrated nitric acid are the only commonly used solvents that will chemically attack it. PEEK is not recommended for use with methylene chloride, dimethyl sulphoxide, or tetrahydrofuran due to a physical swelling effect. PEEK is a hard, yet slightly flexible polymer.

Measurements in hydrofluoric acid are not possible because of the glass prism in the cantilever holder. Measurements in toluene are possible in the closed configuration when the black Viton™ membrane is used.

The newly designed fluid cell proves to be sturdy and easy to assemble.

4 SUMMARY AND CONCLUSIONS

A fluid cell tailored for investigations in varying tribologically relevant environments, e.g. at extreme mechanical and chemical conditions (Figs 2 to 5), was developed. Samples of various shapes and sizes can be investigated in controlled environments, be they fluid (e.g. solvents) or gaseous (e.g. corrosive gases).

The design of the fluid cell makes it easy to construct additional sample holders to accommodate an even wider range of samples of various shapes and sizes.

First results of AFM nanotribology experiments using this fluid cell are presented (Figs 8 to 11).

Among the systems of interest are additives diluted in solvents adsorbing to surfaces and spreading and persistence of ionic liquids on tribologically stressed surfaces [**15**].

To allow for faster scanning, future models of the modified fluid cell shall have optimized mass and still be mechanically stable and thereby allow for faster scanning.

Further developments will include a heating stage and the possibility to change environments while measuring.

The heating stage will be an immersion style heating element that symmetrically heats the surrounding environment for performing experiments in gases or fluids at elevated temperature. The possibility to heat samples is especially interesting for nanotribological performance tests of lubricants and additives at environmental conditions as they occur in the engine.

The four fluid exchange ports (Luer fittings) in the base of the fluid cell allow for nanotribological experiments under dynamic conditions (e.g. continuous increase of additive concentration).

The extended fluid cell seems fit for a multitude of tribological measurements.

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