PROPOSITION DE THÈSE
(Allocation de recherche ministérielle, présidentielle)

Sujet à pourvoir avant fin juin 2018
Prise de fonction à partir d'octobre 2018

Nanotribology of Triboactive Surfaces – Molecularly-assisted Tuning of Friction Laws in a Multi-asperity Tribocontact

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Context:

The design and control of materials at the nanoscale are the foundation of many new strategies for energy generation, storage and efficiency. Friction is an important limitation of energy efficiency performances in MEMS/NEMS [1] whereas it is the primary mean to create energy in new triboelectric nanogenerators (TNG) – *ie.* nanodevice used for energy harvesting [2]. In this framework, multi-asperity nanotribology studies are needed to develop a fundamental understanding of interfacial phenomena where frictional behavior is controlled by interactions between nano-asperities [2,3]. Controlling these interactions is clearly the first *step* for designing *triboactive* surfaces – *ie*, surfaces in which frictional behavior can be controlled *in situ* by means of external stimuli [3]. A promising way consists to apply a suitable stimulus – *eg.* thermal [3, 4], electrical [5, 6] or electromagnetic [7, 8] – on grafted self-assembled monolayers (SAMs) in order to change in real time their dissipated behavior within the contact.

However, the *real* friction laws occurring on the asperity's scale – especially their evolutions over time and over multiple asperities – need to be known to control friction when stimulus is applied. In practice, this complicated assessment is often ignored by assuming that the friction is uniformly shared on the whole nano-asperities which constitutes the so-called *real contact area*. The frictional behavior of a *single* asperity is then commonly assessed by Lateral Force Microscopy and supposed constant over time and well-described by various relationships – *eg*, Coulomb's dry friction, Stokes' viscous friction or Mindlin's partial slip [9-12]. Unfortunately, this classical approach usually fails when dealing with MEMS involving multi-asperity contact because each asperity finally displays its *own* frictional law which is intrinsically connected to its contact radius to sliding amplitude ratio [13]. Thus, the knowledge of the single asperity's friction law appears to be useless especially for grafted self-assembled monolayers because their frictional behavior is mainly controlled by their entropy variations – *ie*, a collective behavior connected with both the sliding amplitude and velocity [14]. On the contrary, knowing the *continuous* variations of the friction laws – as a *multiscale* approach – of stimuli-activated surfaces seems to be a great interest for designing efficiency MEMS or TNG because these laws can be accurately tuned by specially designed or tailored molecules [15, 16].

Objective

In this context, the goal of the PhD thesis will be to develop new kinds of *triboactive* surfaces [3, 15, 16] by using grafted self-assembled monolayers displaying suitable functional groups. SAM will be grafted in liquid medium or in vapor phase. So far, thermal-controlled triboactive surfaces have been successfully tested and validated by using OTS self-assembled monolayers [3] and OTS nano-patterned self-assembled monolayers [16], respectively. A step further will be crossed in this thesis by investigating electromagnetic stimulus in order to develop UV-beam photo-actived triboactive surfaces. For instance, azo-benzene self-assembled monolayers displaying various functional groups seem to be excellent candidates for this purpose. These molecules will be able to be synthesized in our group by the F. Chérioux team [8, 27].

Methodology

The apex of an AFM has commonly been used from decades for studying the frictional laws at the nanoscale [1, 9-12]. However, it is now accepted [3, 11, 12, 15, 17-21, 26] that the assessed friction level with this approach has little to do with the one obtained in real microsystems. The main reason is linked to the so-called *PV limit* – where *P* is the *average contact pressure* and *V* the *sliding speed* – which is not in the same order for MEMS and AFM [18]. This means that molecular scale test methods which duplicate the operating *P-V* space of MEMS are needed for accurately studying the tribological behavior of MEMS. Hence, the main originality of this work comes from both the equipment and methodology that will be used for studying the evolution of friction laws of *triboactive* self-assembled monolayers: indeed,

- first, an original *multi-asperity* nanotribometer has been specifically designed for this purpose in collaboration with J-M Friedt (co-supervisor) from Time-Frequency department [13, 15] in order to match the *PV* limit of classical MEMS. This equipment is based on a quartz-crystal resonator, which is able to work in air, liquid and vacuum [13, 15,18]. The *multi-asperity* contact is simulated by using either: (i) a *millimetric* rough ball or (ii) various *micro-beads* falling onto the grafted resonator in order to dynamically change the *real contact area* during the test. Interactions between the grafted quartz and nano-asperities will be studied over a wide amplitude range – from 0 to 50 nm – with an induced sliding velocity lying from $mm.s^{-1}$ to $m.s^{-1}$ which actually is in the range of actual MEMS or TNG one [18, 22].
- second, our original methodology does not need to make any assumption about the form of the friction law which is expected. Indeed, frictional behavior of self-assembled *triboactive* monolayers can be accurately studied by fitting the evolution of slip-time *vs.* quartz amplitude because there is a direct analogy between this relationship and the one describing the evolution of the friction force with respect to the maximum surface speed (v) at the midpoint of the crystal reciprocating motion [23]. Hence, evolution of the frictional behavior with respect to any external stimulus can be modeled as a generic power law – *ie*, $F_t \propto v^n$ [24] – where n is able to continuously change with the mechanical power injected within the tribocontact. As a result, usual friction laws – as Coulomb (n=0), Stokes (n=1) or Mindlin (n>1) – naturally appear as boundary cases but are never fixed as an assumption.

Thus, *multi-asperity* friction laws will be accurately tuned in this work by specially designed or tailored molecules [15]. In order to bridge the gap between these fundamental investigations and their potential applications in MEMS, a *home-made* numerical simulator has been created to test the dynamics of the friction laws with respect to the external stimuli by using XCOS/Scilab software and the MODELICA language [25]. This simulator will be extended to take into account the effect of the electromagnetic stimulus on power-controlled dissipative laws.

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Background	Master degree or equivalent degree in physical-chemistry, surface science, or nanophysics
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