**Monitoring the dynamics of confined mesoscopic fluids with phase-locked-loop acoustic sensing**

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**A. SCIENCE and TECHNOLOGY UNDERLYING THIS PROPOSAL**

**A.1 Scientific questions addressed in the proposal: The unique physical properties of mesoscopic fluid films**

The physical properties of mesoscopic fluids adsorbed at substrates or confined between solid surfaces differ greatly from those measured in their bulk form.[[1]](#endnote-1),[[2]](#endnote-2) For example, the effective shear viscosity is enhanced, viscoelastic relaxation times are prolonged,[[3]](#endnote-3) they reveal different phase diagram[[4]](#endnote-4) (boiling at lower temperatures, ice formation at room temperature[[5]](#endnote-5),[[6]](#endnote-6)), and the so called hydrophobic interaction manifests at distances well beyond commonly accepted molecular interaction ranges.[[7]](#endnote-7)

But what is the physics behind such unique dynamic behaviors displayed by mesoscopic fluid films? Could it be that *molecular ordering* develops in the region adjacent to the constraining surface boundaries[[8]](#endnote-8) and the resulting non-uniform density (along the normal direction to the surface) becomes the basis for establishing new properties? But, even if so, would that be the only reason? What about the role of the unavoidable *presence of ions*? (Even pure water contains an equilibrium concentration of H3O+ and OH-, although as small as 10-7M).[[9]](#endnote-9),[[10]](#endnote-10) On the other hand, what would be the effects of an eventual presence of *micro- or nano-cavities inside the fluid*, which may form from fluctuation always occurring in a thermodynamic system? A group of such wandering cavities may lead to an apparent long-range of liquid-substrate interaction.[[11]](#endnote-11),[[12]](#endnote-12) This line of reasoning can also leads to a feasible explanation of other mesoscopic fluids phenomena. For example, considering that the probability for the occurrence of cavity fluctuations decreases with decreasing volumes of a liquid, a *metastable* thermodynamic liquid state may developed when a deeply negative pressure (relative to the outside atmospheric pressure) develops, for example, inside a water meniscus bridging a solid nano-sized asperity and a flat substrate; hence a small (heat) perturbation would cause the *trapped water to boil*.4

On the other hand, there is no adequate theoretical explanation yet for the *ice formation at room temperature* in meniscus bridges.4,[[13]](#endnote-13) Still experimental results, obtained by scanning a graphite sample with a sharp probe (2.5 nm/s scan velocity and 5-30% relative humidity RH range), reveal pronounced stick-slip motion in the force loops with a period of 0.4 ± 0.1 nm, very different from the 0.25 nm distance typical for graphite but close to the 0.45 nm lattice constant of hexagonal ice.3,5 Also, the measured two-second time response of the meniscus (to a sudden change in the probe’s motion) is too long compared to the expected microseconds to milliseconds for the formation of a capillary neck via adsorption of water molecules from the water vapor at room temperature and RH 50%;[[14]](#endnote-14),[[15]](#endnote-15) but if we accepted that the condensed water meniscus “immediately” converts into ice, the time scale for ice rearrangements by plastic deformation would be much slower than liquid water.3 Ice formation at room temperature between a tip and a flat gold surface under the effect of very low electric fields has also been reported; 6 and that once formed confinement may not be needed.13

On another aspect, what about the *nature of the fluid itself* ? Would films made of water molecules or larger organic molecules (like octamethylcyclo-tetrasiloxane, OMCTS) behave the same way? Maybe their peculiar group organization (further influenced by the neighboring substrate geometry) would play an important role. Water, for example, with its ubiquitous hydrogen bonding, is considered as a giant molecule, conforming around substrates. Such a conformational ordering would depend on the space available between two interacting substrates and quantified in term of its entropy. The latter would then have a crucial effect on the water-mediated interaction between solid surfaces; for if a lower density in the gap were more favorable in entropic terms, then an attractive force between the solid surfaces would result. In fact, the latter argument is typically used to explain the working mechanism behind the long-range (sometimes greater than 20 nm) hydrophobic interaction.[[16]](#endnote-16) Molecules like OMCTS (non-polar, quasi spherical, ~ 9Å diameter), on the other hand, do not have such a cooperative gigantic organization; hence its dynamic response to confinement between solid surfaces may be different.

**A.2 The relevance of gaining a better understanding of mesoscopic films properties**

Studies of mesoscopic fluid films are relevant to technological areas like adhesion, wetting processes, and nanotribology in general (as there has been considerable effort to develop thin-film coatings to eliminate capillary adhesion between components, and to reduce corrosion and wear).[[17]](#endnote-17),[[18]](#endnote-18) They are also important for understanding the rigidity and flow behavior of granular materials[[19]](#endnote-19),[[20]](#endnote-20) and ceramics,[[21]](#endnote-21) in which deformation occurs by means of the shearing of thin interfacial layers at grain or phase boundaries. They can also lead to the implementation of a better modeling of bio-membranes,[[22]](#endnote-22) gain understanding of water mediated hydrophobic interaction (which mediate the synchronized traffic of fluids in biological membranes)[[23]](#endnote-23), and potentially shed lights on the dynamics of proteins’ folding unfolding processes.

This proposal aims to attain an understanding of interfacial tribology phenomena, focusing on the potential role played by the fluid film trapped between solid surfaces in relative motion. (The analytical acoustic tool to monitor the dynamics of such a mesoscopic liquid is introduced in Section A.5 below). In particular, we are interested in understanding how does *wear-free* *friction* work. Could it be that energy is dissipated via phonons (*i.e*. energy transmitted in the form of sound waves originated in the confined liquid and coupled to the sliding substrate?)17,[[24]](#endnote-24) Support for this view can be found in molecular dynamics (MD) simulations studies of the *phononic mechanism.*[[25]](#endnote-25),[[26]](#endnote-26) Briefly, a rigid crystalline substrate produces a periodic potential  on the adsorbed molecules (here *z* is the coordinate along the axis perpendicular to the substrate surface; ***r*** is the lateral coordinate.) As the substrate shakes laterally and harmonically, it produces deformations on the adsorbate. If the layer followed a similar harmonic motion (*i. e*. no deformation, as is likely to happen if the adsorbed layer were in a solid state), then there would be no dissipation of energy. But if the adsorbed layer were close to a liquid state, anharmonic oscillations (i.e. out of phase with the substrate motion) would lead to a draining of energy.[[27]](#endnote-27) That is, in the phononic mechanism, dissipation of energy arises from substrate-induced deformations in the adsorbate and anharmonic coupling between phonon modes.[[28]](#endnote-28) This proposal puts emphasis on the hypothesis that friction has its origin in the *phase la*g between the sliding solid surfaces and the response of the fluid trapped in between. (The proposed *Phase-lock-loop acoustic feedback* technique to measure this phase lag is described in Section B.1 below.)



A systematic study of the fluid films includes the use, in this proposal, of substrates with different hydrophobic/hydrophilic characteristics, as a way to evaluate the influence of the nature of the substrate boundaries on the fluid dynamics response to shear motion. This procedure can lead to interrogate the nature of the hydrophobic force itself. The latter refers to the *interaction between molecules or between surfaces in water, often stronger than their attraction when in free space.*[[29]](#endnote-29)Although the ‘hydrophobic’ term means ‘water fearing’, the interaction between a hydrophobic molecule (typically a non-polar molecule incapable of forming hydrogen bonds) and water is actually attractive (due to the van der Walls forces, as occur with any other two molecules with induced electrical dipoles); but hydrophobic interaction, it turns out, is simply stronger than what is expected from traditional continuum models (van der Waals, DLVO[[30]](#endnote-30)). Its nature, however, is a matter of controversy; after 30 years of efforts, the search for the hydrophobic force law continues).7 Still, a trend of consensus exists that the force between hydrophobic surfaces manifests differently within three different regimes:29,[[31]](#endnote-31)

*i*) From 100 to 1000 of angstroms, the attractive force is dominated by electrostatic domains present on the approaching surfaces and/or the bridging of vapor cavities[[32]](#endnote-32) (described within the context of capillary forces).[[33]](#endnote-33)

*ii*) In the 15 to 150 angstroms range, a long-range hydrophobic *force* is possibly due to the ‘proton-hopping’ polarizability of water. (Proton-hoping in water is inferred from the fairly rising-trend of the water’s dielectric constant upon freezing, contrasting the abrupt fall of  observed in other polar liquids. An abrupt fall indicates that the contribution to  from thermal rotation of the dipolar molecule has stopped. The high polarizability of water is believed, then, to arise from the proton hopping along the H-bond network29).

*iii*) In the range below 10-15 angstroms a *short-range hydrophobic force* is related to water structuring effects associated with surface-induced changes in the orientation and/or density of water molecules and H-bonds at the water–hydrophobic interface. Some consider this regime to be the true range of the hydrophobic interaction. Since the force is typically detected by monitoring the deflection of the spring supporting one of the surfaces, this *short-range regime of strong interaction* is typically *inaccessible* tohigh lateral resolution tools like *atomic force microscopy* (*AFM*). The shortcoming comes from the fact that an AFM-probe is inherently unstable, as the cantilever will snap into or out of contact with a surface whenever the gradient of the force between the tip and the sample exceeds the cantilever spring constant *k* (of few tens of N/m).[[34]](#endnote-34) In contrast, the SANM technique employed in this proposal does not have such a limitation (it uses a probe with effective spring constant practically infinite along the vertical direction, and ~20,000 N/m along the lateral direction, as described in Section A.5 below). Hence, SANM is more suitable for interrogating the hydrophobic interaction at very short probe-sample separation range.

**A.3 Context: The emphasis on the study of interfaces**

In spite of a standing interest, the dynamics, thermodynamics, and the molecular structure of fluids confined to nanometer-sized regions are not yet well understood at thefundamental level. Efforts to elucidate this problem can be traced to developments in the colloid science field (the study of heterogeneous systems that behave as springy liquid and sticky solid, hence no classifying within the standard solid, liquid, or gas phases). For the past 70 years, the theoretical framework guiding the progress in this area of soft condensed matter has been dominated by the Deryaguin, Landau, Verwey, Overbeek theory (a bottom-up approach theory based on the addition of pair-wise interactions subsequently integrated all over the constituents parts),30 and later by the Lifshitz theory (dealing with interactions across vacuum,[[35]](#endnote-35) subsequently extended to include interactions between the surfaces of colloidal particles separated by an intervening liquid medium[[36]](#endnote-36)) a top-down approach where the measured bulk electrical susceptibilities are incorporated into the molecular constituents interactions. Both approaches attained notable achievements but applied to relatively limited cases. For the majority of cases under realistic experimental conditions (no uniform density, granular media, high concentration of ions), the models become mathematically more difficult, or specific problems had to be fitted with so many parameters that the power of making prediction for different situations is lost. As a matter of fact, the field has been experiencing new revisions in the last decade, as revealed in the refreshing reference by B. W. Ninham and P. Lo Nostro.10 The revisions respond to the need for better addressing, in particular, the heterogeneous characteristic of real substances, the role of ions (Hofmeister effect),9,10 and the effects of cavitation.11,12

One aspect of these limitations is that the old thermodynamic theories have been constructed based on theoretical abstractions applicable to homogeneous materials (to make the theory more mathematically tractable). To remediate this situation, part of the new revision in colloidal science focuses on the study of phenomena occurring near interfaces, where the gradient of density (or other thermodynamic properties) changes drastically only along the direction perpendicular to the interface. Such an ideal situation should display mechanisms similar to the way by which, for example, a liquid terminates at a boundary where it breaks into vapor; it is for this reason that the study of dynamic processes at interfaces is appealing. This point is pertinent to the objectives of this proposal, which aim at the study of mesoscopic films at surfaces (as detailed below).

**A.4 Standard surface characterization techniques**

For the characterization of phenomena occurring at interfaces, the surface force apparatus (SFA)[[37]](#endnote-37) stands out for the pioneering results measuring forces between parallel surfaces separated by distances down to the Angstrom level.[[38]](#endnote-38),[[39]](#endnote-39) In 1982, SFA measured an attractive force *F* = 0.14 e-D/(1.0 nm) N/m between two hydrophobic cylindrical surfaces of radius *R*, for separation distances *D* in the 0–10 nm range.[[40]](#endnote-40) Modified SFA versions allow studying the dynamic of fluids under oscillatory shear.[[41]](#endnote-41),[[42]](#endnote-42) Succinctly, the SFA uses lubricated contacts between atomically-smooth mica surfaces mounted on crossed half-cylinders that laterally slide against each other. The deflections of springs attached to the half-cylinders measure the friction forces[[43]](#endnote-43) under static[[44]](#endnote-44) and dynamic[[45]](#endnote-45) conditions. Notice, however, the indirect nature of the measurement; the dynamic of the fluid is inferred from the mechanical response of the external spring. Also, inherent to its setup, the SFA does not provide lateral resolution close to the nanometer level.

Another important techniques is the quartz microbalance (QM), which exploits the low dissipation internal energy of a single crystal quartz to sense the slippery motion of adsorbed molecules, the latter causing a broadening in the frequency-response of the (5–10 MHz) crystal’s resonance peak.[[46]](#endnote-46) QM has revealed that, contrary to what a macro scale experiment interpretations would suggest, solid films slide more readily than liquid films.[[47]](#endnote-47) The results have been interpreted in terms of the phononic friction mechanism24,[[48]](#endnote-48) (Fig. 1 above). The technique, however, does not offer nanometer-sized lateral resolution, and it is limited to investigate relatively small friction forces so that sufficient sliding (of the adsorbed molecules relative to the QM surface) can occur.

Atomic force microscopy(AFM) brings atomic resolution to the analysis of surfaces.[[49]](#endnote-49) A pyramidal-shape probe is dragged along the surface while its lateral bending, caused by the probe-specimen frictional force is monitored with a laser beam reflecting from the probe. The smaller the bending experienced by the probe, the lower the frictional force.[[50]](#endnote-50),[[51]](#endnote-51) However, similar to asurface force apparatus setting, the technique senses the effects that surface interactions cause on the probe only, while the response from the mesoscopic fluid (trapped between the probe and the substrate) is lost or inferred only from models. (The new SANM acoustic technique described below aims to correct this shortcoming). The AFM probe also suffers from force calibration issues[[52]](#endnote-52) and, particularly, from instabilities.[[53]](#endnote-53) In fact, the spring constant of the AFM probe (being no so rigid, typically few tens of N/m) suffers from snap-in motion (abrupt downward deflection towards the surface) when the probe is being approached to the substrate, which makes difficult to interpret the probe’s response, particularly at very short probe-sample distances where the interaction is stronger than what the AFM probe can discern. (In contrast, the SANM probe is more stable and has greater sensitivity in this short range region closer to the surface; see Fig. 2).

Notice, in none of the three techniques mentioned above the response from the fluid is probed directly. Monitoring *simultaneously* the effects that surface interactions have on both the *probe* and the *fluid layer* would be highly desirable, since a potential phase difference between these two oscillatory motions could reveal important working principles of interfacial (*i.e*. wear-less) friction. Aiming to fulfill such a capability motivated the creation of the SANM technique described below.

**A.5 Shear-force Acoustic Near-field Microscopy (SANM)**

More recently, the PI introduced Shear-force Acoustic Near-field Microscopy (SANM) for directly monitoring, via acoustic transducers, the dynamics of mesoscopic fluids trapped between two nanometer-sized solid boundaries under relative shear motion.[[54]](#endnote-54),[[55]](#endnote-55) SANM differs from other ultrasonic techniques that are based on direct solid-solid contact between the probe and the substrate,[[56]](#endnote-56) including those approaches where the probe dithers perpendicular to the sample’s surface[[57]](#endnote-57) or is kept stationary while an ultrasonic wave is applied to the sample.[[58]](#endnote-58),[[59]](#endnote-59)



**Fig. 2** **Monitoring the acoustic response from confined mesoscopic fluid trapped between solid surfaces in relative motion.** **Left:** The apex of a laterally-oscillating tapered probe is brought into shear interaction with an adsorbed mesoscopic fluid film, thus engendering an acoustic wave that couples to the substrate, travels through the substrate bulk, and is finally detected by an acoustic transducer. **Right:** SANM signal (red-color trace) monitors the acoustic response from the mesoscopic fluid as the confinement of the fluid is gradually reduced. The additional concurrent detection of the probe’s mechanical oscillations (green-color trace) allows a comparison between the two (probe and fluid) oscillatory motions. For demonstration purposes, metallic probe and metallic sample were used to monitor their eventual mechanical contact with a contact current measurement (blue trace). Notice the detection of acoustic SANM-signal even when there is not mechanical contact between the probe and the solid substrate. The SANM signal is also more sensitive when the probe is closer to the sample’s surface, a region in which other techniques, like AFM, presents shortcomings.

SANM was demonstrated in 2005 independent of a similar experimental setting introduced in 1989 that aimed principally at lateral scanning imaging applications, and whose working mechanism was attributed to the dynamic changes of the gas surrounding the probe.[[60]](#endnote-60) In contrast, SANM exploits the fact that an acoustic transducer (attached underneath a stationary substrate, as shown in Fig. 2) has sufficient sensitivity to detect acoustic waves engendered at the matrix of the fluid layer trapped between the *oscillating nanometer-sized apex-probe* and the *sample surface*; such capability had been overlooked in the past. The acoustic waves are driven by the apex-probe, whose mechanical oscillations are also monitored (simultaneously) in the SANM setup. This dual capability offers an opportunity to measure the eventual phase-lag of the fluid’smotion relative to the moving solid apex boundary (this is one of the main tasks pursued in this proposal), which could contribute in understanding the adhesive irreversibility (or hysteresis) involved in tribology phenomena, as it was addressed in Section A.2 above.

About the nanometer analysis capability of SANM: Fig. 2 shows that the generation of acoustic waves occurs even when there is not mechanical contact between the probe and the solid substrate (the latter would trigger the appearance of tunneling current signal, blue trace in the figure), and that the probe amplitude decreases at smaller probe-sample separation distances. This result suggests a distance dependent viscosity of the trapped mesoscopic fluid, which should result in a very localized propagation region (or decaying length) of the sound waves. The closer the probe to the surface, the more localized (and stronger) damping effects, but still the acoustic excitation able to couple to the substrate, from which it propagates towards the acoustic sensor. This implies that the nanometer-sized analysis capability of the mesoscopic fluid in the SANM is retained, particularly when the robe is closer to the substrate, which is the region we want to investigate.

The relevance of SANM measurements can be assessed *a*) within the context of nanotriblogy phenomena studies (access to the fluid motion response would allow comparing its phase-lag response relative to the oscillating probe’s boundary surface, which is believed to be key in understanding the irreversible character of nanotribology phenomena, as addressed in Section A.2 above);[[61]](#endnote-61) and *b*) its potential to investigate interactions between hydrophobic surfaces at very short distances (capitalizing on the fact that the acoustic technique displays highest sensitivity at very short probe-sample separation distances (Fig. 2), precisely where atomic force microscopy[[62]](#endnote-62),[[63]](#endnote-63) becomes less reliable due to the relatively lower spring constant of AFM probes (~ 10 N/m).;[[64]](#endnote-64) hence SANM offers a suitable complementary alternative. SANM takes advantages of its sturdy tuning fork probe (very high spring constant *k=*20,000 N/m) that simultaneously displays very low dissipation characteristics (*Q ~* 2000).

In summary, the dynamics of fluids at, or confined between, solid surfaces (particularly hydrophobic surfaces) presents an interesting rainbow of fundamental and challenging questions.1-7 Despite tremendous efforts, there does not exist yet a general theory able to make predictions under varying circumstances even though a drastic revival of the field has occurred in the last decade.10 In one approach, the study of mesoscopic fluid films at surface and interfaces appear to be a good starting step towards tackling (later on) more complicated geometries. Through this proposal, SANM embraces this strategy and attempts to contribute via answers from a nanometer scale perspective, giving emphasis to the direct monitoring of the fluid dynamic response with acoustic sensors. The latter has not been tried before.

**B. AIMS**

**B.1 Measurement of fluids’ phase-lag response to shear interaction: Phase-lock-loop acoustic feedback**

We will integrate *phase-locked-loop* (PLL) feedback control[[65]](#endnote-65) into our existent in-lab constructed SANM system. The purpose is to provide a *dynamic* *phase reference* (*i.e*. a phase reference that changes in a predictable way and in real-time in response to the probe-fluid interaction) so that a clear phase-difference can be measured between:

*i*) the phase of the PLL-controlled driving voltage (*i.e*. the source that drives the probe’s lateral oscillations and engenders an acoustic wave at the mesoscopic fluid film); and

*ii*) the phase of the acoustic wave detected at the transducer located beneath the sample substrate.

 

**Fig. 3** Phase-locked-loop (PLL) feedback-control for generating acoustic waves by shaking a mesoscopic fluid with a TF-probe. The probe’s oscillatory motion is maintained at a fixed reference phase (**probe) while the probe vertically approaches the sample (*i.e*. while gradually restricting the confinement of the fluid trapped between the probe and sample). The PLL feedback-control achieves the constant phase condition by varying the frequency of the driving voltage *V*drive until the probe reaches a resonance motion (90o lagging phase relative to *V*drive). The phase of the probe motion (kept fixed by the PLL action) will be compared with the simultaneously acquired phase of the acoustic waves (*SANM*) sensed by the acoustic transducer located beneath the sample. (The synchronous detection of *SANM* is not shown in the figure).

The eventual phase-lag of the fluid (acoustic signal phase) relative to the oscillating apex (phase of the driving voltage) will be measured at different probe-substrate distances. PLL-SANM capitalizes on the high stiffness (~ 20,000 N/m) of the TF holding the probe (hence uncontrollable snaps of the tip towards the surface, as occurs in AFM, are avoided), as well as on the highest sensitivity of the SANM signal at smaller probe-sample separation distances where the viscoelastic properties of the trapped fluid appear to be more evident. The latter, in particular, makes more feasible the PLL-SANM attempts to measure the eventual phase-lag between the probe and fluid motions.

Figure 4 shows schematically the corresponding experimental implementation. A piezoelectric tuning fork (TF), with a sharp stylus attached to one of its tines, is electrically driven at its resonance frequency (~ 32 kHz), which results in 4nm-amplitude oscillations when the tip is located far away from the substrate. Under this resonance condition, the electrical signal response from the TF is 90o out of phase with respect to the driving voltage (*V*drive). When the apex of the probe is brought into shear interaction with the fluid film adsorbed on the surface, the lateral oscillations serve to engender an acoustic signal. Because of the tip-fluid interaction (assumed to be viscoelastic), the TF output signal (pin #1 in the figure) undergoes a phase change because the probe is now out of resonance. Such a change in phase is exploited by the PLL section of the circuit where a voltage controlled oscillator (VCO) responds by adjusting the frequency ( *f* ) of the driving voltage (*V*out) until the laterally oscillating probe reaches again a resonance condition (*i.e*. the phase signal at pin #1 is back lagging 90o with respect to the driving voltage) at the new probe-sample distance. The net effect is that *the probe’s motion* (*i.e. the source responsible for exciting the acoustic wave*) *is kept at a fixed phase value with respect to the driving voltage*. This way, variations in the independently monitored SANM acoustic phase-signal can be attributed solely to the characteristic response from the mesoscopic fluid film (where the acoustic wave is generated.) This capability for direct phase-lag measurement of the fluid motion relative to the probe’s motion would constitute the distinct feature of the PLL-SANM to be undertaken in this proposal.

The rich analysis available from SANM is illustrated by the fact that SANM is not restricted to single point measurements when quantifying the complex viscosity of a fluid; lateral mapping of the fluid film’s properties is also possible. To activate this extra SANM operational mode, pin-out #4 from the PLL is selected instead of pin #3 (Fig. 3), which allows maintaining the probe’s resonance frequency at a predetermined constant value (see set-point *f* ), while the probe is laterally scanned. The automated changes in the voltage Vz voltage (or required changes in the sample’s vertical position) required to keep the resonance frequency constant will reflect the unevenness of the viscoelastic properties. (For control experiment atomically flat samples will be used, that way the viscoelastic properties can be easier contrasted).

Instead of tracking the TF’s amplitude by electrical means (pin #1 in Fig. 3), one can alternatively use the whispering gallery acoustic sensing (WGAS) signal55 (pin #2); pin #1 goes to ground in this case. WGAS is another acoustic technique, recently introduced by the PI, that monitors the amplitude of the TF’s oscillations via an acoustic sensor judiciously placed on the perimeter of the SANM microscope frame.55 WGAS overcomes the adverse effects of the TF’s intrinsic capacitance that prevents a direct measurement of the mechanical motion of the TF when electrically monitoring the amplitude of the TF; hence acousto monitoring via WGAS offers better metrology capability.

**B.2 Monitoring the elastic and inelastic components of shear-force interactions,**

We will exploit the PLL-SANM capabilities to discriminate the elastic (conservative) and inelastic (dissipative) components of the interaction between the probe-apex and the adsorbed mesoscopic fluid (we will use water and OMCTS films). Indeed, since the probe is driven at its resonance frequency at all time for any arbitrary probe-sample distance, *i*) changes of the TF signal amplitude can be ascribed to dissipative components of the interaction, while *ii*) any blue-shift in the frequency will be related to the presence of conservative forces.

For the analysis of the experimental results, we will resort to models typically used in studies with interfacial microcopy that use quartz tuning forks as probes. It turns out that a simple forced harmonic oscillator model describes well the dynamics of TFs.[[66]](#endnote-66) First, for the TF we are currently using, the equivalent spring constant is calculated according to *K*stat=(*E*/4)*w*(*t/L*)3=26**103*N/m*. Then, to determine the amplitude of the probe’s mechanical oscillations *uo* we use our calibrated piezo-electro-mechanical coupling constant =6.5**10-6*C/m*.[[67]](#endnote-67) From the harmonic motion approximation we estimate the TF output current to be detected by our meter *I*=2**(2*f* )*uo*; at the resonance frequency *f* (typically around 32 kHz) the change in current that we measure is *I*=2.5 nA/nm. For a probe of quality factor *Q=1800*, this current/amplitude calibration allows to estimate the corresponding lateral forces involved *F*=*K*stat *u*o/*Q*, or 15 nN/nm. Recently, we have improved our detection system and reached a 50 pA pk-to-pk noise level, equivalent to *20* *pm* amplitude of oscillation, and 350 pN lateral force. (Increasing the gain of our amplifier from 106 to 108 we expect to increase further force sensitivity). We are able then to monitor accurately the lateral forces involved in the SANM experiments.

The damping (** and elastic (*k* characteristics of the fluid film can be calculated by comparing the equation of motion for the probe interacting with the fluid layer, *M*+ *M*(*o+*)**+(*ko+k*)*x*=*F*e*it*, with the one when the probe is far away, *M*+*Mo*+*kox*=*F*e*it*. The equation is deceptively simple but *k* and ** can be a complicated function of several parameters, including temperature, pressure, and speed of the probe’s motion. Considering resonance condition in both cases, respectively, one obtains *=o* [(*f*o *x*o / *f x*) - 1]. Also, a comparing(*2f* )2*=*(*ko+k*)*/M*  with(*2fo*)2*=ko /M* leads to *k=*[(*f /fo)2-* 1]*ko*. Hence, measuring the resonance frequency *f* and amplitude of oscillation *x* at different probe-sample distances, one can obtain the elastic and damping characteristics of the fluid film.Further*,* since the SANM signal will be acquired simultaneously, the distance-dependent fluid film’s acoustic response can then be contrasted with the solid-probe’s damping and elastic behavior.

Complementing this analysis, we will attempt to verify an interdependent relationship between the damping and elastic characteristics of the fluid, modeled through a slightly different treatment of the probe’s equation of motion. Starting with *M*+ *Mo* + *kox* = *Fdrive* + *Fprobe-fluid* (*x* is the probe’s displacement), we express the damping effect of the fluid on the probe as *Fprobe-fluid* = – *M,* where ** stands for the fluid velocity, which takes into account that the layer is also in motion. That is, the damping force is not given simply by –*M* anymore, but proportional to the relative velocity of the probe with respect to the in motion fluid. Now, since the displacement of the fluid layer is induced by the motion of the probe, it is plausible to assume , where  is a complex factor accounting for the phase-lag between the probe and fluid motion (** constitutes the phase-lag to be measured with the PLL-SANM approach described in Aim B-1 above). This gives, . Notice that the second term in the expression for  contributes with an effective spring constant  affecting the motion of the probe, and revealing that it is related to the dissipative interaction. Measurement of *k*, ** (as detailed in the previous paragraph) and ** (via PLL-SANM)) at different probe-sample distances would allow verifying this relationship and establishing the complex fluid character of the mesoscopic fluid film.

Further verification of the models can be attained performing additional experiments at different pressure (to vary the film thickness) and temperature (to change the viscosity) conditions. Budget permitted, we plan to integrate SANM capability into an ultra-high vacuum chamber. The ultrahigh vacuum is to achieve a reference condition in which, eventually, no fluid film is present so the results corresponding to gradual formation of fluid films, under different pressure levels, can be contrasted. The chamber fame is requested in this proposal, but the other vacuum components will come from a refurbished ISI DS-130C SEM system currently available at the PI lab.

**B.3 Investigation of phase transformations induced by confinement**

The combined PLL-SANM, able to track variations in the damping and elastic properties of the fluid films (as outlined in Section B.2 above), is suitable for investigating the potential liquid-to-solid phase transformation that trapped mesoscopic fluid may undergo as a consequence of gradual increase of confinement, which is is relevant to tribology studies,[[68]](#endnote-68) with engineering perspective applications.[[69]](#endnote-69) We will test water and OMCTS films.

The selection of water is based on recently reported evidence that it behaves like glue between a tungsten tip and a graphite surface,3 as addressed also in Section A.1 above. Further, water nucleating between the tip and the surface due to capillary condensation rapidly transforms into ice at room temperature.3,5 Ice formation between a tip and a surface with the assistance of an electric field at room temperature has also been reported;6 and that once formed the mere presence of a single interface with the substrate (*i.e*. under no confinement) may be sufficient.13 These recent results add to the intriguing behavior of water, frequently causing controversial arguments; indeed it had been proposed in the past that water would stay liquid and retain a viscosity close to the value for bulk water, even under extreme confinement.[[70]](#endnote-70) As far as this proposal is concerned, we realized that, based on the fact that the associated thermodynamic transition is dictated by the natural formation of a meniscus around the tapered probe, there is no need of special additional geometry changes of the probe (or any other special alignment) in the SANM setup to perform the corresponding frequency modulation acoustic measurements.

On the other hand, for fluid films composed of larger molecules, a parallelism between the probe’s truncated shape and the flat sample would be required (implementation of such a requirement into the SANM is detailed in the next paragraph) to better test eventual molecular organizations on the surface and its corresponding effects on the acoustic signal. We will test non-polar organic octamethylcyclo-tetrasiloxane (OMCTS) liquid films, trapped between a truncated-apex probe (see Figs 6B and 6C)[[71]](#endnote-71) and an atomically flat (mica) solid boundary. Confinement-induced phase transition in OMCTS has been reported in the literature,[[72]](#endnote-72),[[73]](#endnote-73) but it is subjected to controversy.[[74]](#endnote-74),[[75]](#endnote-75) In a SANM setting, where the detected acoustic signal depends on the constitutive nature of the fluid-like film, offers a supplementary alternative way to monitor either a sudden first-order phase transition or, instead, a gradually continuous OMCTS transition to a glassy state as a function of increasing confinement.

To improve the SANM measurements one of the objectives of this proposal consists of exploring methods to achieve a parallelism between a truncated apex probe (Figs. 5B and 5C) and an atomically flat substrate. Borrowing ideas from the SFA method (mentioned in Section A.4 above), we plan to use a near-field optical probe (Fig. 5C) as a SANM probe, and resort to Fringes of Equal Chromatic Order (FECO)31,[[76]](#endnote-76) as a way to attain surface parallelism condition at probe-sample separation distances close to sub-nanometer level.38,[[77]](#endnote-77) Our ability to fabricate truncated probes of arbitrary cross section areas (Fig. 5B), we will try first micron-sized cross section areas but then gradually decreasing its dimension until FECO analysis is still allowed. On the other hand, the fine angular degrees of freedom required to maneuver the probe’s angular position (to reach parallelism condition guided by FECO) will be achieved through the use of a five-electrode piezo scanner tube to which the tuning fork (holding the probe) is attached to. Finally, the wavelength-dependent transmitted fringes of constructive interference, resulting from multiple reflections in the probe-sample gap, will be redirected by the beam splitter towards a spectrometer (Fig. 5).



**Fig. 5**. **Left:** A variety of probes fabricated at the PI’s laboratory. *A*:Uncoated tapered glass fiber.*B*: Tapered (glass or metal) probe with a truncated flat apex (fabricated using an FIB system).[[78]](#endnote-78) *C*: Aluminum-coated tapered fiber-glass with an aperture at the flat apex.[[79]](#endnote-79) **Right:** Proposed implementation of Fringes of Equal Chromatic Order (FECO) method31,76 to attain parallelism between the flat section of a truncated near-field optical probe and an atomically flat mica substrate. Shifts in the wavelength-dependent interference fringes, due to the changes in the gap distance *h*, are sensitively monitored by a spectrometer. The inset on the top-right side shows the fringe pattern observed in a spectrometer, and the surface configuration, which may be deduced therefrom.31

This arrangement constitutes a very sensitive method to track parallelism as well as probe-sample distance variations. We expect the diagonal interface of the beam splitter not to affects drastically the acoustic signal reaching the acoustic transducer, given the fact of the large acoustic wavelength (~ few cm at 32 kHz) compared to the 5 mm thick beam splitter. We also expect the thickness of the beam splitter no to affect detrimentally the acoustic signal; in previous measurements we have tested samples with thickness larger than 5 mm without observing any detrimental in the detection of the acoustic signal.[[80]](#endnote-80) Once an acoustic signal is coupled on the top side of the surface, it just propagates down to the acoustic sensor without detrimental to its intensity.

Finally, it is worth mentioning the potential outgrowth of SANM (not detailed in this proposal) as a result of a successful implementation of this proposal. For example, by using a near-field optical probe (a metal-coated glass fiber tapered probe with a nano-sized aperture at the apex)[[81]](#endnote-81) in the SANM experimental setting, the mesoscopic fluid could be additionally analyzed optically[[82]](#endnote-82), namely though Raman spectroscopy. This would constitute a versatile outgrowth of an Optical/SANM for characterizing mesoscopic films.

**C. BROADER IMPACT**

The PI, recipient of thePSU 2005 Civic Engagement Award “Excellence in Faculty/Community Partnership” and the PSU 2006 John Eliot Allen “Outstanding Teaching Award,” will capitalize on the acoustic characterization of mesoscopic fluids proposal to continue the support of outreach activities in three important areas:

**C.1** P**romoting community service, mentoring of high school students, and diversity**  In coordination with the Center for Academic Excellence at PSU,[[83]](#endnote-83) Dr. La Rosa and his enthusiastic PSU graduate students have held annual presentations on technology oriented topics at elementary and high school institutions. These activities promote the development of a spirit of community service on PSU students and, at the same time, help to attract the best high-school students into nanotechnology career programs.

Diversity is one of the most important institutional initiatives undertaken by Portland State University, supporting a campus environment that acknowledges, encourages and celebrates differences.[[84]](#endnote-84) Currently, out of four graduate students under the direction of the PI, two of them are female. In the past the PI mentored Jesús Ramirez, a high school student of Latino origin from Molalla High school (Summer 2003 and 2004). The PI’s support for diversity is also evidenced in Fig. 6, showing mentored high school students from different ethnic background. Through the current proposal, the PI plans to continue promoting diversity initiatives, and help fulfill PSU institutional initiatives.

**C.2 Expanding the instructional and educational services provided by the PSU Portland Nanoscience and Nanotechnology Academy (PNNA)**

The PI is one of the main organizers of the multidisciplinary PNNA group at PSU (www.pdx.edu/pnna), whose goal is to promote collaboration among traditional disciplines of science and engineering. PNNA activities focus in three main areas: teaching, sharing a network of research equipment, and collaboration. Availability of research equipment is vital for the development of nanotechnologies. The SANM, while being operated and maintained by the PI, will become part of the network of shared analytical equipment available to PNNA members. It will be made available also for PH 510/CH-545 NanoFab, which is a hands-on training course (for graduate and undergraduate students) on the fabrication and characterization of nanomaterials.

**C.3 Strengthening international research collaboration with the National University of Engineering, Lima, Perú**

The PI views collaboration with research centers in South America as an activity that, if it were more widely spread, could contribute to the process of stabilizing the economies of developing countries. Nanotechnnology, expected to shape global economics in a near future, is going to increase the already wide technological gap between developed and developing countries (along with the consequent social implications). One objective of this proposal is to promote the assimilation of molecular dynamics simulations to study mesoscopic films at the national University of Engineering. Dr. Javier Solano, Director of the School of Computer Science, one of the four branches within the Faculty of Science, has agreed to collaborate with the PI in this mission. We expect to initially support a couple of Peruvian students (with a total budget not exceeding $3k per year). These students will be working under the direct supervision of Dr. Solano. PSU will benefit from the skills and expertise developed by the Peruvian researchers, have access to well-qualified professionals, and enhance the international dimensions of Portland State University.

**E. TIMETABLE OF PROJECT DEVELOPMENT AND EVALUATION**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Year** | **1** | | **2** | | **3** |
|  | | | | | |
| **O**  **B**  **J**  **E**  **C**  **T**  **I**  **V**  **E**  **S** | Upgrading existent hardware of the Shear force Acoustic Near-field Microscope (SANM). | | Implementation of the  FECO technique to ensure parallelism between a truncated-cone probe and a sample’s substrate. | | Measurement of the fluids’ phase-lag response to shear interaction. |
| Implementation of phase-locked-loop (PLL) feedback into the SANM (operation at ambient condition). | | | |
| Design and construction of a vacuum compatible SANM microscope stage. | | Integrating a new SANM stage into a UHV chamber (complemented with components of an existent refurbished ISI-SEM). | | |
| Undergraduate student is trained in the use of a thermal vacuum evaporator to fabricate near-field optical probes, which will be used as SANM probes.  Investigating hydrogen terminates surfaces as a reference system. | | Investigation of phase transformation induced by confinement  (working with organic octamethylcyclo-tetrasiloxane OMCTS liquid films). | | Characterization of films at different vacuum conditions. |
| Experimental verification (at ambient conditions) of the fluid’s viscoelastic model proposed in AIM B.2. (Relationship between its damping constant **f and its effective elastic *k*f characteristics). |
| The PI mentors two high school students on the following activities: Whispering Gallery Acoustic sensing, and arduino-microcontrollers in the fabrication of SANM probes. | | | | |
| Integration of “Acousto-characterization of mesoscopic fluid films” into the syllabus of PNNA-NanoFab course (offered during the Spring terms at PSU). | | | | |
| Establish international collaboration with Dr. Javier Solano’s Computer Simulation Group, National University of Engineering, Lima, Perú.  Project: Numerical simulation studies of complex fluids. | | | | |
|  | | | | | |
| **E V A L U A T I O N** | | | | | |
|  | Graduate student completes Ph.D. degree.  New graduate student is trained in the operation of the SANM. | Publication of papers on:  - SANM with FECO control.  - Acousto monitoring phase transformation of fluids under confinement. | | “PLL-acoustic characterization of mesoscopic fluid films” published in the Review of Scientific Instrument journal. | |
| High school student Sydney Hung, together with the PI, publishes a paper in a peer review journal. Topic: Whispering gallery acoustic sensing with improved sensitivity. | | | | |
| The hands-on training course NanoFab (offered during the Spring terms at PSU) includes acoustic techniques as a topic in its syllabus. | | | | |
| Dr. Solano’s group (National University of Engineering, Lima-Perú) and the PI”s group publish a joined manuscript in a peer reviewed journal. | | | | |
|  | | | | | |

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