

**Final Report for Period:** 09/2011 - 08/2012**Submitted on:** 01/31/2013**Principal Investigator:** Riedo, Elisa .**Award ID:** 0706031**Organization:** Georgia Tech Research Corp**Submitted By:**

Riedo, Elisa - Principal Investigator

**Title:**

Liquid Dynamics in Nano-Confined Geometries: Nanohydrodynamics

### Project Participants

#### Senior Personnel

**Name:** Riedo, Elisa**Worked for more than 160 Hours:** Yes**Contribution to Project:**

#### Post-doc

**Name:** Lucas, Marcel**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Marcel Lucas has worked as supervisor for Tai-de Li, in terms of training in the lab, and scientific discussions. Also, he has worked on the project for the creation of chemically nano-patterned surfaces by TCNL. He was supported by DOE and NSF-STC funds.

**Name:** Kim, Suenne**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Suenne joined my group as a Post Doctoral Fellow in January 2009. She is participating in the supervision of one PhD student involved in this project. Suenne is partially supported by NSF.

**Name:** Chiu, Hsiang-Chih**Worked for more than 160 Hours:** Yes**Contribution to Project:**

#### Graduate Student

**Name:** Li, Tai-De**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Tai-de Li is the main player of the research project supported by this NSF grant. He is in fact the first author of the paper published this year in Phys. Rev. Lett.

**Name:** Ortiz, Deborah**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Deborah Ortiz (a new female and minority graduate student) will be the successor to Tai-De Li in this project. Right now, she is learning how to use an AFM and she is studying the topic. She will be paid by this grant starting from this summer. Deborah was supported by the School of Chemistry.

**Name:** Wang, Debin**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Debin Wang has worked on the project for the creation of chemically nano-patterned surfaces by TCNL. He was supported by NSF-STC funds.

**Undergraduate Student**

**Name:** Kickhofel, John

**Worked for more than 160 Hours:** No

**Contribution to Project:**

John worked on the contact angle measurements. He was not financially supported.

**Name:** Dunnells, Andrew

**Worked for more than 160 Hours:** No

**Contribution to Project:**

Andrew developed the software for correcting the thermal drift. He was not financially supported.

**Technician, Programmer****Other Participant****Research Experience for Undergraduates****Organizational Partners**

**University of Basel**

**International Centre for Theoretical Physics**

**University of Lyon**

**Other Collaborators or Contacts**

I collaborate with Prof. Lyderic Bocquet from the University of Lyon (France).

I also work with the University of Basel, the International Centre for Theoretical Physics in Italy, and EPFL in Lausanne.

**Activities and Findings****Research and Education Activities:****RESEARCH ACTIVITIES:**

The viscoelastic dynamics of nano-confined water is studied by means of atomic force microscopy (AFM). We observe a nonlinear viscoelastic behavior remarkably similar to that widely observed in metastable complex fluids. We show that the origin of the measured nonlinear viscoelasticity in nano-confined water is a strain rate dependent relaxation time and slow dynamics.

We have been working on modifying the wettability of surfaces at the nanoscale with a resolution below 15 nm. These surfaces will be later on used to conduct fundamental studies on liquid properties at the interface with a nanostructured surface.

**EDUCATION ACTIVITIES:**

During 2007-2008, I mainly worked on this project with two graduate student, Tai-De Li, who has been working with me since the starting of my previous NSF grant. He graduated in June 4th 2008 with a thesis on 'AFM experiments on nano-confined fluids'. Now, he is a Post Doctoral Fellow at the University of California, Berkeley.

Since January 2008, a new PhD student, Deborah Ortiz, joined my group to work on the continuation of this project.

I was a co-organizer of the Conference 'Nano and Giga Challenges in Electronics, Photonics and Renewable Energy', Hamilton, Ontario, Canada, August 10-14, 2009.

I was a co-Organizer of the Focus Topic "Tribophysics" of the Division of Materials Physics for the 2010 March Meeting of the American Physical Society (APS).

I participated to a Career Panel at the 2008 NSF-STC retreat in Atlanta, and to the WIC (Women in Chemistry) & CMDITR - Georgia Tech Leadership Lunch 'Female Faculty Work Life Balance' in October 2008.

Also, I have started a series of workshops, held twice a year, once in Georgia Tech (organized by me) and once in Emory (organized by Prof. Weeks), that brings together researchers (faculties, post docs, graduate and undergraduate students) with an interest in soft materials, molecular forces, biophysics, molecular electronics and fluid dynamics to discuss their work and explore collaborations. The 1st Southeast Meeting on Soft Materials, on May 9, 2008, had more than 100 participants from GT and Emory, since then every year this workshop bring hundreds of students and faculties at GT. For more information about the 'Soft Materials' community at GT please check at <http://www.softmaterials.gatech.edu>.

At present this series of workshop, held yearly in May, is well established and other faculties have already step up to organize the workshops.

### **Findings:**

By measuring the viscoelastic modulus of nano-confined water at different frequencies and strains, we find that the intrinsic relaxation time of nano-confined water is in the range 0.1-0.0001 s, orders of magnitude longer than that of bulk water, and comparable to the dielectric relaxation time measured in supercooled water at 170-210 K.

The wettability of a thin polymer film was modified twice by thermochemical nanolithography. By means of a first local chemical modification induced by an atomic force microscope tip heated to 110°C, hydrophilic patterns are written over an originally hydrophobic polymer surface. By further heating to 190°C, a second chemical modification reverses the local wettability change introduced by the first chemical modification. This write-read-overwrite capability can be particularly useful in the design of complex nanofluidic devices.

Finally we have performed a series of experiments which indicate that the interfacial viscosity of water for gaps below a few nanometers depends dramatically on the slippage of water at the stationary surface. By using an atomic force microscope (AFM), we have measured the lateral viscous force,  $F_L$ , experienced by a nano-size tip in water while it is sheared parallel to a very smooth solid surface at a velocity  $v_{shear}$ , as a function of the tip-surface distance,  $d$ . These viscous force curves,  $F_L(d)$ , strongly depend on the wetting properties of the solid surfaces, with force values varying from one surface to another one up to one order of magnitude for the same tip-surface distance. It is well known that a liquid which wets well a surface, usually does not slip at the boundary with this surface. More precisely, recent molecular dynamics calculations find a universal relationship

between water slippage and surface contact angle (where higher contact angles correspond to higher hydrophobicity). We have thus investigated the possibility that the observed surface-dependent variations in the viscous forces are related to the boundary slippage. Since a Mica surface is known to have zero boundary water slippage, we have considered  $FL(d)$  on mica as the zero slippage curve,  $F0L(d)$ , and we have fit the lateral viscous forces for other different surfaces with the equation  $F0L(d)/(1+b^*/d)$ , where  $b^*$  is a free fitting parameter accounting for slippage. This equation is derived very simply from the Newtonian definition of viscosity, considering that the slip length  $b$  is the extrapolated distance into the solid where the velocity of the liquid goes to zero; for a linear velocity profile we can write  $v_{shear} \propto (d + b) \cdot \dot{\gamma}$ . This simple equation can perfectly account for the different  $FL(d)$  curves measured on six different surfaces. Moreover, the fitting slip parameter  $b^*$  is found to increase almost linearly with the static contact angle of the corresponding surface, in agreement with the above mentioned molecular dynamics simulations, further supporting the idea that the interfacial viscosity of water is intimately related to the slip. Finally, the obtained slip parameter increases with the shearing rate with the same linear dependence in all the surfaces investigated here.

### **Training and Development:**

Learning how to use atomic force microscopes, contact angle meters, and software development for instrument/electronics interface.

Development of new characterization techniques and nanolithography AFM-based methods.

All my students are trained in a very interdisciplinary environment where surface chemistry/physics, fluidynamics and mechanics are all key ingredients.

All my students/post docs participate and give presentation at National Meetings.

### **Outreach Activities:**

See before in the EDUCATION ACTIVITIES.

### **Journal Publications**

Li, TD; Riedo, E, "Nonlinear viscoelastic dynamics of nanoconfined wetting liquids", PHYSICAL REVIEW LETTERS, p. , vol. 100, (2008). Published, 10.1103/PhysRevLett.100.10610

Wang, DB; Szoszkiewicz, R; Lucas, M; Riedo, E; Okada, T; Jones, SC; Marder, SR; Lee, J; King, WP, "Local wettability modification by thermochemical nanolithography with write-read-overwrite capability", APPLIED PHYSICS LETTERS, p. , vol. 91, (2007). Published, 10.1063/1.281640

Lucas, M; Leach, AM; McDowell, MT; Hunyadi, SE; Gall, K; Murphy, CJ; Riedo, E, "Plastic deformation of pentagonal silver nanowires: Comparison between AFM nanoindentation and atomistic simulations", PHYSICAL REVIEW B, p. , vol. 77, (2008). Published, 10.1103/PhysRevB.77.24542

Wang, DB; Kim, S; Underwood, WD; Giordano, AJ; Henderson, CL; Dai, ZT; King, WP; Marder, SR; Riedo, E, "Direct writing and characterization of poly(p-phenylene vinylene) nanostructures", APPLIED PHYSICS LETTERS, p. , vol. 95, (2009). Published, 10.1063/1.327117

Lucas, M; Zhang, XH; Palaci, I; Klinke, C; Tosatti, E; Riedo, E, "Hindered rolling and friction anisotropy in supported carbon nanotubes", NATURE MATERIALS, p. 876, vol. 8, (2009). Published, 10.1038/NMAT252

Lucas, M; Wang, ZL; Riedo, E, "Combined polarized Raman and atomic force microscopy: In situ study of point defects and mechanical properties in individual ZnO nanobelts", APPLIED PHYSICS LETTERS, p. , vol. 95, (2009). Published, 10.1063/1.317706

Lucas, M; Gall, K; Riedo, E, "Tip size effects on atomic force microscopy nanoindentation of a gold single crystal", JOURNAL OF APPLIED PHYSICS, p. , vol. 104, (2008). Published, 10.1063/1.303951

Wei, ZQ; Wang, DB; Kim, S; Kim, SY; Hu, YK; Yakes, MK; Laracuente, AR; Dai, ZT; Marder, SR; Berger, C; King, WP; de Heer, WA; Sheehan, PE; Riedo, E, "Nanoscale Tunable Reduction of Graphene Oxide for Graphene Electronics", SCIENCE, p. 1373, vol. 328, (2010). Published, 10.1126/science.118811

Wang, DB; Kodali, VK; Underwood, WD; Jarvholm, JE; Okada, T; Jones, SC; Rumi, M; Dai, ZT; King, WP; Marder, SR; Curtis, JE; Riedo, E, "Thermochemical Nanolithography of Multifunctional a Nanotemplates for Assembling Nano-objects", ADVANCED FUNCTIONAL MATERIALS, p. 3696, vol. 19, (2009). Published, 10.1002/adfm.20090105

Gnecco, E; Riedo, E; King, WP; Marder, SR; Szoszkiewicz, R, "Linear ripples and traveling circular ripples produced on polymers by thermal AFM probes", PHYSICAL REVIEW B, p. , vol. 79, (2009). Published, 10.1103/PhysRevB.79.23542

Deborah Ortiz-Young, Hsiang Chih Chiu, and Elisa Riedo, " Water nano-hydrodynamics: the interplay between boundary viscosity, slip and hydrophobicity", Nature Nanotechnology, p. , vol. , (2013). Submitted,

Chiu, Hsiang-Chih;Ritz, Beate;Kim, Suenne;Tosatti, Erio;Klinke, Christian;Riedo, Elisa;, "Nanotubes: Sliding on a Nanotube: Interplay of Friction, Deformations and Structure (Adv. Mater. 21/2012)", Advanced Materials, p. 2797-2797, vol. 24, (2012). Published,

H.-C. Chiu;S. Kim;C. Klinke;E. Riedo;, "Morphology dependence of radial elasticity in multiwalled boron nitride nanotubes", Applied Physics Letters, p. 103109, vol. 101, (2012). Published,

Hsiang-Chih Chiu;Sedat Dogan;Mirjam Volkmann;Christian Klinke;Elisa Riedo;, "Adhesion and size dependent friction anisotropy in boron nitride nanotubes", Nanotechnology, p. 455706, vol. 23, (2012). Published,

Marcel Lucas;Elisa Riedo;, "Invited Review Article: Combining scanning probe microscopy with optical spectroscopy for applications in biology and materials science", Review of Scientific Instruments, p. 061101, vol. 83, (2012). Published,

Suenne Kim, Si Zhou, Yike Hu, Muge Acik, Yves J. Chabal, Claire Berger, Walt de Heer, Angelo Bongiorno, and Elisa Riedo;, "Room Temperature Metastability of Multilayer Epitaxial Graphene Oxide", Nature Materials, p. 544, vol. 11, (2012). Published,

Suenne Kim;Yaser Bastani;Haidong Lu;William P. King;Seth Marder;Kenneth H. Sandhage;Alexei Gruverman;Elisa Riedo;Nazanin Bassiri-Gharb;, "Direct Fabrication of Arbitrary-Shaped Ferroelectric Nanostructures on Plastic, Glass, and Silicon Substrates", Advanced Materials, p. 3786-3790, vol. 23, (2011). Published,

### **Books or Other One-time Publications**

M. Lucas, T.-D. Li, E. Riedo, "Nanomechanics: Fundamentals and NEMS", (2008). Book, Accepted  
Collection: Nanostructure Science and Technology series  
Bibliography: Springer

D. Wang, V. Kodali, J. Curtis, E. Riedo, "Nanofabrication of Functional Nanostructures by Thermochemical Nanolithography", (2011).  
Chapter in Book, Published  
Collection: Chapter in "Tip Based Nanofabrication: Fundamentals"  
Bibliography: Springer

### **Web/Internet Site**

**URL(s):**

<http://riedo.gatech.edu/>

**Description:**

## Other Specific Products

### **Product Type:**

**Software (or netware)**

### **Product Description:**

Provisional Patent: ?High Resolution Force Curves in Atomic Force Microscopy?. GTRC-ID-4523 (4/15/2008)

### **Sharing Information:**

If any company is interested in commercializing this software we will file a patent, othewise we will share it with others through the web.

### **Product Type:**

**Other inventions**

### **Product Description:**

???Thermally-Activated Chemical Nanopatterning???.

### **Sharing Information:**

Patterning at the nanoscale

## Contributions

### **Contributions within Discipline:**

We have studied the room temperature viscoelastic properties of nano-confined water, finding a slow dynamical behavior similar to that observed in metastable complex fluids. By measuring the viscoelastic modulus at different frequencies and strains, we have found that the intrinsic relaxation time of nano-confined water is about 0.06 s.

We have shown how the boundary viscosity of water strongly depends on the wetting properties of the confining surfaces. This dependence is fully explained by considering water slippage at the stationary solid surface. The boundary viscosity as a function of the gap size for six surfaces with different wettabilities is fitted with a modified form of the Newtonian definition of viscosity, taking fluid slip into consideration. This simple relationship can explain the interfacial viscosity measurements and allows the extraction of a 'slip parameter' for each investigated surface. This slip parameter is found to increase with the hydrophobicity of the solid surface as expected from previous work, bringing the first experimental evidence of the relationship between interfacial viscosity and slip.

We have developed a new technique for the modification of the surface chemistry at the nanoscale. This technique called 'TCNL' can have an impact in biomedicine, biophysics, nanofluidics and nanoelectronics.

### **Contributions to Other Disciplines:**

Our work suggests that confinement defines an effective temperature of the system which is lower than the canonical temperature.

Also, by means of a new technique to control the mechanical drift, we have demonstrated that Atomic Force Microscopy can be an excellent tool to study liquid-solid interfaces, even with sub-nanometer resolution.

See before.

### **Contributions to Human Resource Development:**

The series of workshops 'SouthEast Meetings on Soft Materials' (see section EDUCATION ACTIVITIES) is a great opportunity for graduate and undergraduate students in the Atlanta Metro aerea, including underrepresented institutions, to meet, interact and show their work to

senior established Professors who in turn can offer future positions. Starting in 2009 we also have had industrial partners supporting this initiative.

We also filed a US and international patent on thermochemical nanolithography technique (TCNL) and a company has signed a contract to license this technology.

**Contributions to Resources for Research and Education:**

See previous sections.

**Contributions Beyond Science and Engineering:**

United States Patent Application

Thermochemical Nanolithography Components, Systems, And Methods

Serial No.: 12/791,466

Filing Date: 1 June 2010

**Conference Proceedings**

**Categories for which nothing is reported:**

Any Conference