Final Technical Report for Award DESC0011912

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The George Washington University

"Trimodal Tapping Mode Atomic Force Microscopy: Simultaneous 4D Mapping of Conservative and Dissipative Probe-Sample Interactions of Energy-Relevant Materials"

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I. GENERAL AWARD INFORMATION

1. **Award number:** DESC0011912
   Recipient institution: The George Washington University

2. **Project title:** *"Trimodal Tapping Mode Atomic Force Microscopy: Simultaneous 4D Mapping of Conservative and Dissipative Probe-Sample Interactions of Energy-Relevant Materials"*
   Principal investigator: Santiago D. Solares

3. **Report date:** September 22nd, 2017
   Period covered by the report: July 1st, 2014 through June 30th, 2017

II. RESEARCH ACTIVITIES AND OUTPUT

4. Summary of accomplishments:

The key accomplishments for the project were as follows:

a) Developments in atomic force microscopy methods

Fundamental developments in viscoelastic material imaging:

The multifrequency atomic force microscopy (AFM) methods developed within this project are most useful in the characterization of soft viscoelastic materials. Of particular interest to the Department of Energy are polymer films, such as those used in organic photovoltaic systems. However, the underlying theory to properly interpret AFM measurements for this type of materials is lacking. For this reason, part of the effort in this project was dedicated to the development of a solid foundation for the study of viscoelastic AFM measurements. Two parallel approaches were followed, one numerical and one theoretical-analytical.

Numerical approach: A quasi-3-dimensional (Q3D) viscoelastic model and software tool for use in AFM was developed, which is based on a 2-dimensional array of standard linear solid (SLS) model elements, as illustrated in Figure 1 [Section 5, Ref. b]. The well-known 1-dimensional SLS model is a textbook example in viscoelastic theory but is relatively new in AFM simulation. It is the simplest model that offers a qualitatively correct description of the most fundamental viscoelastic behaviors, namely stress relaxation and creep. However, this simple model does not reflect the correct curvature in the repulsive portion of the AFM force curve, so its application in the quantitative interpretation of AFM experiments is relatively limited. In the Q3D model the use of an array of SLS elements leads to force curves that have the typical upward curvature in the repulsive region, while still offering a very low computational cost. Furthermore, the use of a multidimensional model allows for the study of AFM tips having non-ideal geometries, which can be extremely useful in practice. Examples of typical force curves were constructed for single- and multifrequency tapping mode imaging, for both of which the force curves exhibit the expected features. Finally, a software tool to simulate amplitude and phase spectroscopy curves was developed, which can be easily modified to implement other controls schemes in order to aid in the interpretation of AFM experiments, and which is provided as supporting information for the (open source) journal publication [Section 5, Ref. b]. In a subsequent publication, the Q3D model was enhanced with in-plane surface elastic forces which can be approximately related to a two-dimensional (2D) Young’s modulus. Relevant tip-sample interaction cases were studied for single- and multifrequency intermittent-contact AFM imaging, with focus on the calculated surface indentation profiles and tip-sample force curves, as well as their implications with regards to experimental interpretation. As before, the software tool was made available to the public through an open source journal publication [Section 5, publication c].

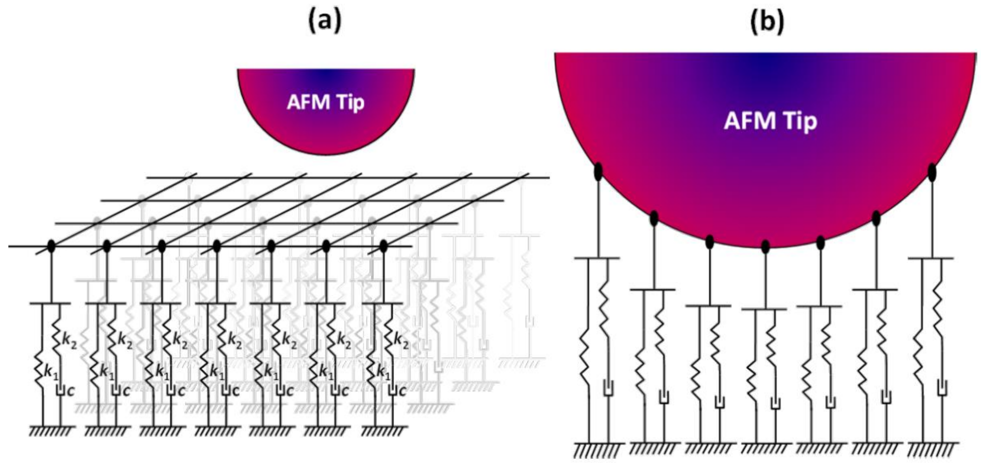

Figure 1. (a) Illustration of AFM tip approaching a 2-dimensional array of SLS models; (b) illustration of AFM tip interacting only with the SLS models directly below it, and interacting to a different depth with each element, as dictated by its geometry.

Theoretical-analytical approach: In a first theoretical step, the physics of the AFM tip interacting with a *generalized* viscoelastic sample containing an *arbitrary* number of characteristic times (Figure 2), were studied for the case when the cantilever's base is driven with constant velocity toward the sample. The results showed that this mode of operation, often called static force spectroscopy (SFS), can be harnessed to thoroughly analyze time-dependent viscoelastic information frequently overlooked in experiments. The solution of previous authors who have studied the standard linear solid model was generalized, and a solution applicable to any linear viscoelastic model was offered. This generalization is crucial for the prediction of the model's response over wide ranges of time-scale. As a demonstration, successful predictions of harmonic functions (e.g., loss tangent) over a wide frequency range were obtained through analysis of simulated SFS results. In addition, it was shown that analysis through the generalized solution and previous expressions is no longer valid when the tip-sample force does not grow linearly in time, so an alternate route for extracting the viscoelastic information was also delivered, which does not rely on the force linearity assumption. Despite the large amount of theoretical content in this work (included for theoretical rigor's sake) [Section 5, Ref. h], the practical user can also benefit from the new procedures offered and the corresponding extensive explanations published. In a second step, the contact problem of a flat-end indenter penetrating intermittently a generalized viscoelastic surface, containing multiple characteristic times was explored [Section 5, Ref. k]. This problem is especially relevant for nanoprobing of viscoelastic surfaces with the standard tapping mode AFM imaging technique or with multifrequency AFM. By focusing on the material perspective and employing a rigorous rheological approach, analytical closed-form solutions were derived, which provide physical insight into the viscoelastic sources of repulsive forces, tip-sample dissipation and virial of the interaction. A systematic comparison was offered with respect to the well-established standard harmonic excitation, which is the case relevant for dynamic mechanical analysis (DMA) and for AFM techniques where tip-sample sinusoidal interaction is permanent, such as contact-resonance AFM. This comparison highlighted the substantial complexity added by the intermittent-contact nature of the interaction, which precludes the derivation of straightforward equations as is the case for the well-known harmonic excitations. The derivations offered were thoroughly validated through numerical simulations. Despite the complexities inherent to the intermittent-contact nature of the technique, the analytical findings highlight the potential feasibility of extracting meaningful viscoelastic properties even with simple tapping-mode AFM.

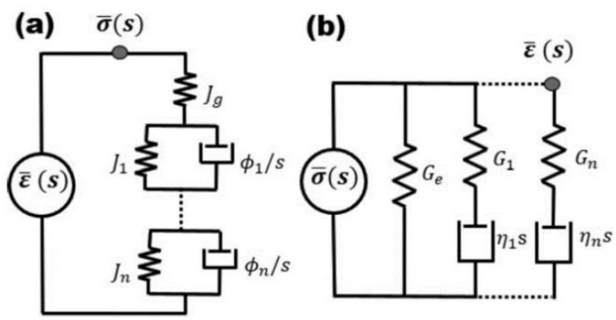

Figure 2. Mechanical model diagrams representing the relationship between stress and strain in the complex plane for a linear viscoelastic material with multiple characteristic times. (a) Generalized Voigt or Kelvin model, (b) Generalized Maxwell or Wiechert model, both describing arrheodictic (there is no steady-state flow) behavior. J_n and G_n refer to the compliance and modulus of the n-th spring, respectively. ϕ_n and η_n refer to the fluidity and viscosity of the n-th dashpot, respectively. J_g and G_e refer to the glassy compliance and rubbery modulus, respectively. In (a) the Laplace transformed strain $\bar{\varepsilon}(s)$ is regarded as the excitation and the transformed stress $\sigma(s)$ as the response; in (b) the opposite occurs. To the PI's knowledge, these are the most sophisticated models so far in the modeling of viscoelastic AFM imaging.

Developments in multifrequency atomic force microscopy:

In line with the project topic, several advancements were accomplished in the field of multifrequency AFM:

Systematic approach for the optimization of the excitation frequency in bimodal AFM: The cantilever excitation frequency and tip free oscillation amplitude are two critical imaging parameters in tapping-mode AFM, and in any multifrequency AFM method derived from it. In general, the excitation frequency is selected to be 'near' the measured resonance frequency of the probe, but there is no previously established systematic approach for making that choice. In this work it was shown that the choice of excitation frequency can play a very significant role in the characterization of viscoelastic materials, even when considering small deviations with respect to the resonance frequency. Additionally, analytical expressions were offered and verified through experiments and numerical simulations, which offer guidance for selecting the drive frequency that maximizes probe sensitivity. The new approach was demonstrated experimentally through single-eigenmode and bimodal AFM measurements performed on spin-coated Nafion® proton exchange thin films. The results show that very often, the phase contrast channel is optimized by selecting an excitation frequency that is *not* necessarily at or near the free resonance frequency [Section 5, Ref. a].

Systematic approach for the optimization of the excitation frequency for the special case of piezo-electrically driven AFM in liquid environments: Imaging in liquid environments is critical for the study of solid-liquid interfaces (e.g., battery electrode morphologies and reactions), but is very challenging due to the high damping exerted by the fluid on the probe, which leads to different dynamics than in low-damping environments such as gases. In this activity, a method for guiding the selection of the microcantilever excitation frequencies in low-quality-factor bimodal AFM experiments was proposed. Within the new method, the compositional contrast frequency is selected based on maximizing the derivative of the phase shift with respect to the drive frequency, observed during a tuning curve. This leads to different frequency choices and significant differences in the observables with respect to the customary practice of selecting the drive frequencies based on the amplitude peaks in the tuning curve. The corresponding journal publication [Section 5, Ref. d] illustrated the advantages and disadvantages of the new approach by imaging an atomically flat calcite surface with single-eigenmode tapping-mode AFM in water, but driving a higher eigenmode instead of the fundamental eigenmode, and by imaging a polytetrafluoroethylene thin film with bimodal AFM, also in water.

Multimodal atomic-resolution methods combining flexural and torsional cantilever eigenmodes: A new multifrequency method was introduced, which involves the excitation of flexural and torsional eigenmodes of the microcantilever probe in liquid environments (see Figure 3). The flexural and torsional deflection signals are mostly decoupled in the majority of commercial AFM setups, so they can be relatively easily recorded and processed. The use of torsional modes provides additional surface information at the atomic scale, with respect to flexural mode imaging alone, although the flexural modes are the only ones capable of 'true' atomic resolution imaging. In the experiments, the torsional modes were observed to be particularly sensitive to protruding oxygen surface atoms on the calcite (101-4) plane. The high lateral resolution capability of the flexural modes, combined with the high sensitivity of the torsional modes to specific surface features in liquid environments, can thus offer the means of observing chemical contrast at the atomic level using purely mechanical measurement AFM techniques, even in the absence of tip functionalization [Section 5, Ref. f].

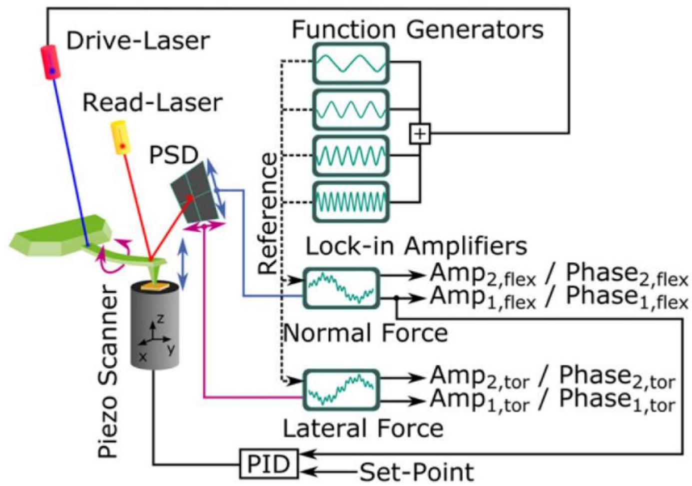

Figure 3. Schematic diagram of multimodal AFM for exciting and demodulating two flexural and two torsional modes of the cantilever (four eigenmodes in total). The signals of four separate function generators are used to excite the cantilever at two different flexural and two different torsional eigenmodes simultaneously. The cantilever is driven photothermally using a blue (405 nm) laser while its response is measured using a laser beam deflection setup with a red (850 nm) laser and a four-segment photodiode. In our setup, an amplitude modulated PID-feedback controlled the fundamental flexural mode amplitude by adjusting the base of the cantilever while the other modes are excited in open-loop (OL). The implementation of the topography feedback using the fundamental flexural mode is customary in standard tapping-mode AFM and in most multifrequency AFM methods.

b) Characterization of energy-relevant materials and systems

In keeping with the project objectives, various sample systems relevant to the mission of the Department of Energy were studied:

Characterization of surface nanobubbles: Imaging of soft matter with atomic force microscopy (AFM) is challenging due to tip-induced deformation, which convolutes with the measurement. The challenges are generally more serious in liquid environments due to a severe loss of sensitivity of the vibrating microcantilever to external forces, as well as due to the presence of undesirable mechanical resonances when piezoelectric excitation systems are used. Furthermore, the choice of imaging parameters can have a significant impact on the quality of the results, such that the customary practices used for tuning the cantilever are not always appropriate. This activity explored the influence of the chosen drive frequency on the imaging of ultrasoft matter, using surface gas nanobubbles on gold-coated glass and highly oriented pyrolytic graphite (HOPG) as a test platform [Section 5, Ref. e]. Such systems are relevant, for example, in the study of electrode surfaces. For this study, single- and multifrequency AFM experiments were conducted using both the traditional amplitude-peak method and the recently proposed phase-slope-peak method [Section 3; Section 5, Ref. d] for tuning the cantilever, as well as piezoelectric and photothermal excitation, providing an extensive discussion on the factors governing the level of tip-induced sample deformation and the quality of the phase contrast obtained for each of the methods. The general conclusion is that there is no "one-size-fits-all" approach for tuning the cantilever for low-impact tapping-mode AFM, although rational optimization of the imaging process is generally possible, whereby the choice of the drive frequency plays a prominent role. The physical insight and guidelines provided here can be extremely useful for the gentle imaging of a wide range of gas-liquid interfaces, soft polymers, biological systems and other soft materials in liquid environments. See Figure 4.

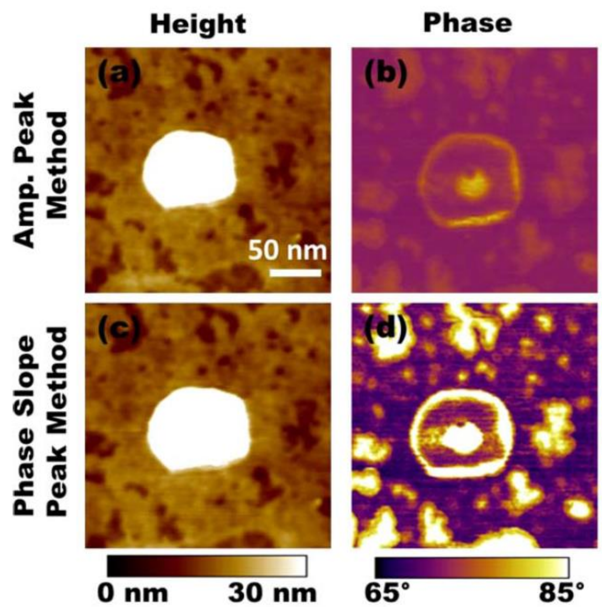

Figure 4. Comparison of images for a nanobubble on a gold-coated substrate for two different excitation frequency selection methods: (a) height and (b) phase images for the amplitude-peak method; (c) and (d) corresponding images for the more sophisticated phase-slope-peak method, respectively. Notice the higher quality of image (d) with respect to image (b).

Nanorheology of Nafion® proton exchange polymer films: Addition of a strong base to Nafion® proton exchange membranes is a common practice in industry to increase their overall performance in fuel cells. This activity investigated the evolution of the nanorheological properties of Nafion® thin films as a function of the casting pH, via characterization with static and dynamic, contact and intermittent-contact AFM. The addition of the strong base KOH caused non-monotonic changes in the viscoelastic properties of the films, which behaved as highly dissipative, softer materials near neutral pH values, and as harder, more elastic materials at extreme pH values. This behavior was quantified through calculation of the temporal evolution of the compliance and the glassy compliance of the surface under static AFM measurements. These observations were complemented with dynamic AFM metrics, including dissipated power and virial (for intermittent-contact-mode measurements), and contact resonance frequency and quality factor (for dynamic contact-mode measurements). The non-monotonic material property behavior was explained in terms of the degree of ionic crosslinking and moisture content of the films, which varies with the addition of KOH. This work focused on the special case study of the addition of strong bases, but the observed mechanical property changes are broadly related to water plasticizing effects and ionic crosslinking, which are also important in other types of films and ion exchange systems [Section 5, Ref. g].

Characterization of diode-like defects in organic photovoltaics: Organic photovoltaic systems comprising donor polymers and acceptor fullerene derivatives have become attractive for inexpensive energy harvesting. Extensive research on polymer solar cells has provided insight into the factors governing device-level efficiency and stability. However, the detailed investigation of nanoscale structures is still challenging. This activity thus focused on the analysis and modification of unidentified surface aggregates on PCDTBT-PCBM active layer films [Section 5, Ref. i]. The aggregates were generated by varying the casting solvent of the film, and were subsequently characterized electrically by Kelvin probe force microscopy and conductive atomic force microscopy (C-AFM), whereby the correlation between local electrical potential and current confirmed defective charge transport for holes, but not for electrons. Bimodal AFM modification confirmed that the aggregates exist on top of the solar cell structure, and was used to remove them and to reveal the underlying active layer. The systematic analysis of the surface aggregates suggested that the structure consisted of acceptor polymer (PCBM) molecules, whereas speculations of their identity based on the sample preparation methods would suggest that they consisted of donor polymer (PCDTBT) molecules. This systematic study, which also included electric field simulations of the electrical measurements with AFM, illustrates the usefulness of the combination of multiple AFM methods with simulations, as well as surface modification with multifrequency AFM, which can shed important light for the proper interpretation of observations regarding organic photovoltaic systems performance (see Figure 5).

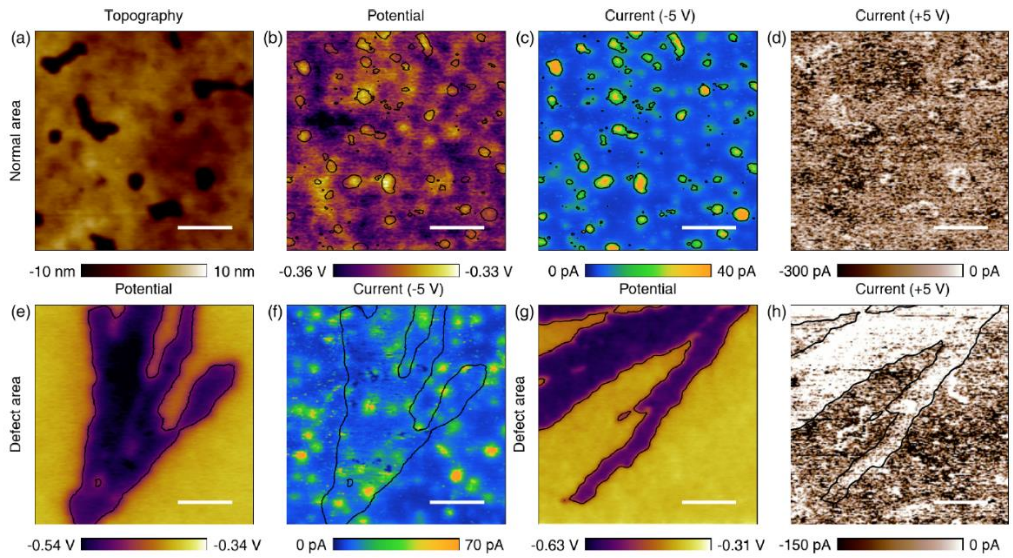

Figure 5. Systematic correlation of the potential and current for normal and defective areas in a PCDTBT-PCBM photovoltaic active layer. (a) Topography of a normal bulk area. (b) Potential of the normal area. (c) Current for the same area measured with forward (−5 V) tip bias. (d) Current of the same area for reverse (+5 V) tip bias. (e) Potential for a defective area containing unidentified surface aggregates. (f) Corresponding forward current. (g) Potential for a second defective area. (h) Corresponding reverse current. Black contour lines highlight the correlation between potential and electron current in (b) and (c) and the defect boundaries in panels (e)–(h). The scale bars are 500 nm.

Development and characterization of nacre-mimetic conductive nanocomposites: Bioinspired design has been central in the development of hierarchical nanocomposites. Particularly, the nacre-mimetic brick-and-mortar structure has shown excellent mechanical properties, as well as gas-barrier properties and optical transparency. Along with these intrinsic properties, the layered structure has also been utilized in sensing devices. This activity extended the multi-functionality of nacre-mimetics by designing an optically transparent and electron conductive coating based on PEDOT:PSS and nanoclays Laponite RD and Cloisite Na+ [Section 5, Ref. j]. The work included extensive characterization of the nanocomposite using transmittance spectra (transparency), conductive atomic force microscopy (conductivity), contact-resonance force microscopy (mechanical properties), and SEM combined with a variety of stress-strain AFM experiments and AFM numerical simulations (internal structure). The nanoclay's response to the application of pressure with multifrequency AFM and conductive AFM was also studied, whereby it was observed that increases and decreases in conductivity can occur for the Laponite RD composites. A possible mechanism to explain the changes in conductivity was offered by modeling the coating as a 1-dimensional multibarrier potential for electron transport, which suggested that conductivity can change when the separation between the barriers changes under the application of pressure, and that the direction of the change depends on the energy of the conducting electrons. Changes in conductivity were not observed under the application of pressure with AFM for the Cloisite Na+ nanocomposite, which has a large platelet size compared with the AFM probe diameter. No pressure-induced changes in conductivity were observed in the clay-free polymer either. See Figures 6 and 7.

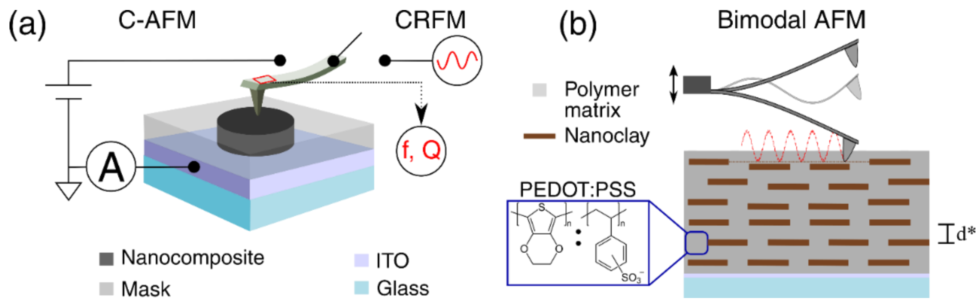

Figure 6. (a) Schematic illustration of the overall sample structure and the consecutive imaging of conductive AFM and contact-resonance AFM. (b) Illustration of the bimodal AFM setup and detailed PEDOT:PSS-nanoclay nanocomposite description, including the expected sample response from the high-pressure treatment (red sinusoidal line).

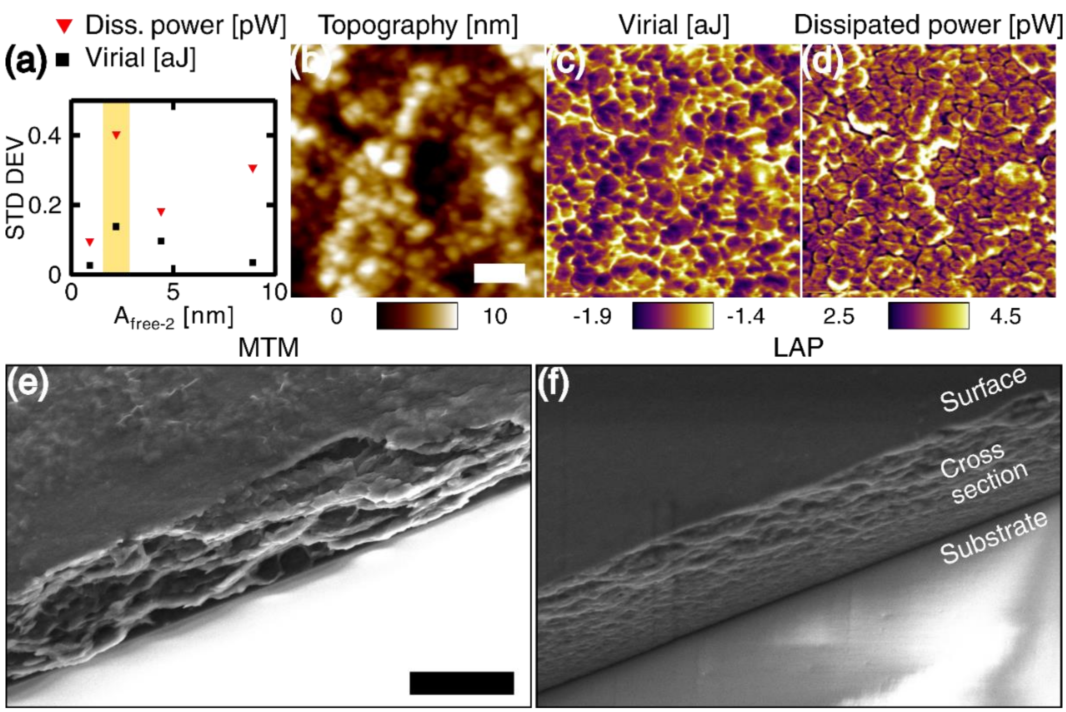

Figure 7. Measurement of virial and dissipated power (conservative and dissipated energy quantities in AFM) for the second eigenmode of the cantilever in bimodal AFM, on the nanocomposite surface of Figure 6 for 33/67 ratio of thin Laponite-RD/PEDOT:PSS. The first AFM eigenmode was operated in repulsive regime (phase below 90 º). The amplitude of the second eigenmode was varied in order to optimize the contrast in the energy quantities summarized in (a), where

the standard deviation of the measurement is plotted against the free oscillation amplitude (a large standard deviation is desired in order to maximize the image contrast). Images b to d (topography, virial and dissipated power) correspond to the condition highlighted by the yellow area in (a). The scale bar (b) is 100 nm. (e-f) SEM characterization of the sample cross section. The scale bar in (e) is 5 μm.

5. List of publications in which DOE is acknowledged:

The journal papers corresponding to this project are the following:

a) Eslami, B.; López-Guerra, E.A.; Diaz, A.J.; Solares, S.D. “Optimization of the excitation frequency for high probe sensitivity in single-eigenmode and bimodal tapping-mode AFM,” *Nanotechnology* **2015,** *26,* 165703 (12pp).

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b) Solares, S.D. “A simple and efficient quasi 3-dimensional viscoelastic model and software for simulation of tapping-mode atomic force microscopy,” *Beilstein Journal of Nanotechnology* **2015,** *6,* 2233-2241.

Acknowledgement text: The author gratefully acknowledges support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences through award DESC0011912.

c) Solares, S.D. “Nanoscale effects in the characterization of viscoelastic materials with atomic force microscopy: coupling of a quasi-three-dimensional standard linear solid model with in-plane surface interactions,” *Beilstein Journal of Nanotechnology* **2016,** *7,* 554-571.

Acknowledgement text: The author gratefully acknowledges support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences through award DESC0011912.

d) Eslami, B.; Solares, S.D. “Experimental approach for selecting the excitation frequency for maximum compositional contrast in viscous environments for piezo-driven bimodal atomic force microscopy,” *Journal of Applied Physics* **2016,** *119,* 084901 (7 pp).

Acknowledgement text: The authors gratefully acknowledge support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DESC0011912.

e) Eslami, B.; Solares, S.D. "Imaging of surface nanobubbles by atomic force microscopy in liquids: influence of drive frequency on the characterization of ultrasoft matter," *Microscopy Research and Technique* **2017,** *80,* 41-49.

Acknowledgement text: The authors gratefully acknowledge support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DESC0011912.

f) Meier, T.; Eslami, B.; Solares, S.D. "Multifrequency force microscopy using flexural and torsional modes by photothermal excitation in liquid: atomic resolution imaging of calcite (10-14)," *Nanotechnology* **2016,** *27,* 085702 (9 pp).

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g) Eslami, B.; López-Guerra, E.A.; Raftari, M.; Solares, S.D. "Evolution of nano-rheological properties of Nafion® thin films during pH modification by strong base treatment: A static and dynamic force spectroscopy study," *Journal of Applied Physics* **2016,** *119*, 165301 (11 pp).

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h) López-Guerra, E.A.; Eslami, B.; Solares, S.D. "Calculation of Standard Viscoelastic Responses with Multiple Retardation Times Through Analysis of Static Force Spectroscopy AFM Data," *Journal of Polymer Science – Part B: Polymer Physics* **2017,** *55,* 804-813.

Acknowledgement text: The authors acknowledge support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award # DESC0011912.

i) Noh, H.; Diaz, A.J.; Solares, S.D. "Analysis and modification of defective surface aggregates on PCDTBT:PCBM solar cell blends using combined Kelvin probe, conductive and bimodal atomic force microscopy," *Beilstein Journal of Nanotechnology* **2017,** *8,* 579-589.

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j) Diaz, A.J.; Noh, H.; Meier, T.; Solares, S.D. "High-stress study of bio-inspired multi-functional PEDOT:PSS/nanoclay nanocomposites using AFM, SEM and numerical simulation," *Beilstein Journal of Nanotechnology* **2017,** in press.

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k) López-Guerra, E.A.; Solares, S.D. "Material property analytical relations for the case of an AFM probe tapping a viscoelastic surface containing multiple characteristic times," *Beilstein Journal of Nanotechnology* **2017,** in press.

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