Nonlinear Dynamics of Nanoscale Systems

Thesis by

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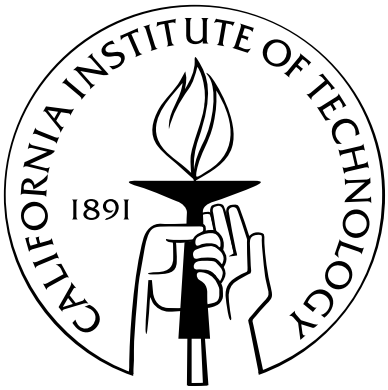
In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy



California Institute of Technology

Pasadena, California

2011

(Defended May 6, 2011)

"The Sun is a mass of incandescent gas..."

—*Why Does the Sun Shine?* by They Might by Giants

"The Sun is a miasma of incandencent plasma. The Sun's not simply made of gas... That thesis has been rendered invalid!"

—*Why Does the Sun Really Shine?* by They Might be Giants

Acknowledgements

I am honored to thank so many people for helping and guiding me over the past years.

I learned a great deal in my previous life in Hideo Mabuchi's lab. Mike Armen and Andy Berglund made great squash partners as well as great tutors, enthusiastically teaching me all about optics and electronics. I really appreciate Ramon van Handel's patience with my questions about Markov processes and the Fokker-Planck equation. Kevin McHale and Asa Hopkins were great office- and benchmates. I also want to thank Tony Miller, John Au, John Stockton, Ben Lev, Nicole Czakon, Gopal Sarma, Orion Crisafulli, and Joe Kerckhoff. The quantitative finance seminar with Luc Bouten and Tim McGarvey was fun and a welcome diversion when I was trying to get over the hump of my third and fourth year, plus I now understand the Ito calculus. Of course, the other member of the Mabuchi lab to remain at Caltech, Sheri Stoll, was both a friend and a resource, and without her I would not know about Liō, the boy who loves giant squid.

A tip from Andy started a collaboration with Kris Helmerson at NIST. It was there I really learned about single molecule microscopy. I thank Kris for hosting me in Maryland for those many weeks. I enjoyed worked closely with Jauyang Tong and Ana Jofre, with whom I spent many hours in a darkened tent trying to catch droplets

of water with a laserbeam. Many thanks to Rani Kishore for working with me to advance the hydrosome project, doing much of the DNA wet work, and teaching me the best ways to prepare pristine samples. It was a shame we could never get things to work completely before Hideo left for Stanford, but my time at NIST also taught me that cutting edge research requires squashing gremlin after gremlin. Otherwise, it would have been done already! I have many thanks for Hideo for supporting me and encouraging me, and I know I have missed out on a lot by not following the lab to Stanford. That said, I have no regrets for staying at Caltech.

I have many people to thank in my second life at Caltech. The members of the Marcus lab, past and present, were great companions at our Friday lunches, Zhaoyan Zhu, Wei-Chen Chen, Yousung Jung, Evans Boney, Maksym Kryvohuz, Nima Ghaderi, and Yun-Hua Hong. I also want to thank Jau Tang for help with the GFPmut2 project and Yanting Wang for doing the simulations for the SFG work. I want to extend extra thanks to Evans and Nima for sharing so many great conversations and for productive collaborations. It is hard to express adequate appreciation for the mentorship and advising from Rudy. Every minute was enlightening and informative, and I was lucky to be able to work with someone so dedicated to his students and supportive of my interests.

In the Fraser lab, I also have many people to thank. Aura Keeter was indispensable for helping me find my way around the lab and helping with maxi-preps and getting machines to work. I extend similar appreciation to Mary Flowers, the lab mom, Kristy Hilands, the former lab administrator, and Pat Anguiano, Scott's admin. I

am indebted to the help from Christie Canaria, who shared so many reagents and protocols with me. I have special thanks for Thai Truong for helping me with the microscopes and many helpful discussions. I also thank Jeff Fingler for our last minute attempts to use OCT to measure the refractive index of zebrafish. It was worth a try. Thanks to Jelena Culic-Viskota for tirelessly working to perfect the SHG nanoparticles. WIthout Andres Collazo, I would not have had access to the House Ear Institute's Zeiss 710, and he was great to talk to while sitting in that dark, cold room. Thanks to my officemates, Mat Barnet, Cambrian Liu, and, recently, Danielle Bower. I would not have even had an office if it weren't for the generosity of Larry Wade, who knew exactly what I was going through when we were both struggling to get things to work. To my closest collaborators, Bill Dempsey and Laki Pantazis, you both taught me a great deal, and I would not be graduating now if it weren't for your help and advice. You have also been good friends, and I was lucky to find such great partners. I also thank the other members of the lab for their support, including Le Trinh, Luca Caneparo, Roee Amit, Max Ezin, Alana Dixon, Greg Reeves, Frederique Ruf, David Huss, David Koos, and Dave Wu. Of course, I extend my deep thanks to Scott Fraser, whose advice and insight proved vital over and over. Without your great sense for experimental design, I would still be shooting lasers at globs of barium titanate, and I am honored that you were willing to support me after Hideo left.

There were many people outside the lab who helped me reach this point. Edgardo Garcia was the right person at the right time to help me, and I'm lucky to have him as a friend. Best of luck in San Jose. Of course, all of my fellow RAs helped me

successfully navigate the world of the Caltech undergraduate housing system. Also, many thanks to Dean Barbara Green, Sue Chiarchiaro, Geoff Blake, and Tim Chang for helping us overcome so many challenges with the students. Ruddock House was our home for three years, and it was an amazing time. We laughed, we cried, and we learned a lot about life. It was the second half of my life at Caltech, outside research, and it was very fulfilling.

I am lucky to have such a loving family to help me through. As a new parent, I am now doubly aware how nurturing and supportive my parents have been at every step of my life. I don't know how they dealt with me, but I am lucky to have them. Of course, it's easy to thank little Leo. There is nothing like coming home to his bright face to help me relax and recharge, and my productivity significantly increased after he joined us. He even literally inspired a section of my thesis, and he is duly noted in that chapter. Last, it is hard to overstate the help I got from my wife and best friend, Jenn. From helping me purify GFPmut2 to supporting our family while I went into hermit mode to write my thesis, she was there every step of the way; and I am lucky to have such a caring companion, and I look forward to spending many future happy years together. This work is dedicated to you. Love, Sq.

Abstract

This work builds theoretical tools to better understand nanoscale systems, and it explores experimental techniques to probe nanoscale dynamics using nonlinear optical microscopy. In both the theory and experiment, this work harnesses nonlinearity to explore new boundaries in the ongoing attempts to understand the amazing world that is much smaller than we can see. In particular, the first part of this work proves the upper-bounds on the number and quality of oscillations when the system in question is homogeneously driven and has discrete states, a common way of describing nanoscale motors and chemical systems, although it has application to networked systems in general. The consequences of this limit are explored in the context of chemical clocks and limit cycles. This leads to the analysis of spontaneous oscillations in GFPmut2, where we postulate that the oscillations must be due to coordinated rearrangement of the beta-barrel. Next, we utilize nonlinear optics to probe the constituent structures of zebrafish muscle. By comparing experimental observations with computational models, we show how second harmonic generation differs from fluorescence for confocal imaging. We use the wavelength dependence of the second harmonic generation conversion efficiency to extract information about the microscopic organization of muscle fibers, using the coherent nature of second

harmonic generation as an analytical probe. Finally, existing experiments have used a related technique, sum-frequency generation, to directly probe the dynamics of free OH bonds at the water-vapor boundary. Using molecular dynamic simulations of the water surface and by designating surface-sensitive free OH bonds on the water surface, many aspects of the sum-frequency generation measurements were calculated and compared with those inferred from experiment. The method utilizes results available from independent IR and Raman experiments to obtain some of the needed quantities, rather than calculating them *ab initio*. The results provide insight into the microscopic dynamics at the air-water interface and have useful application in the field of on-water catalysis.

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Chapter 1

Introduction

The nanoscale is the spatial regime at least 10 times larger than atoms and simple molecules, yet also 10 times too small to be resolved by the unaided human eye. Such small things are often readily disturbed by the constant jostling of their air and liquid environments. A grandfather clock that is 50 nm tall will not tick, no matter how precisely it is machined. A bacteria does not swim by paddling through water like a fish, instead it moves by spinning a flagella. Making things smaller can make them different. Gold, when broken down into 10 nanometer crystals, transforms in color from the familiar shiny metal into a deep red, and silver turns yellow. Hence, nanotechnology is exciting not just because we can make big things smaller but because we can make new things.

A crystal composed of thousands or millions of atoms may have completely differently properties from its isolated constituent atoms and may also be different from a larger version of the same crystals. At first, this would be no surprise to someone like a baker, who transforms unpalatable flour, salt, baking soda, fat, and sugar into delicious doughnuts. But, making a doughnut is a series of chemical reactions, while the changes in size-dependent properties occur spontaneously. A better analogy would be

making a doughnut by cutting it out of a pizza, and suddenly it was sweet and savory, or by squeezing two pieces of rye bread together and ending up with tasty dessert. These metaphors are drawn from examples in this thesis, where we explore how the optical properties of water at the water-vapor boundary are different from those in the liquid bulk. We prove that making a system larger may allow it to oscillate longer and more predictably. Finally, we consider how the microscopic arrangement of protein fibers in muscle interact nonlinearly with laser light, yet a different arrangement of the same proteins on the nanoscale would make such a nonlinear interaction impossible. We use this information to learn more about the organization of muscles on the microscopic level.

Nanoscale systems often contain a limited number of relevant states,[1] and we often want to do something useful with those states, such as operate a motor protein or convert light into electricity. These require highly correlated dynamics that persist in time. Unfortunately, damping by the environment, due to buffeting by solvent molecules, tends to prevent oscillatory dynamics which might be necessary for successful operation of nano-machines or chemical systems. The second law of thermodynamics implies that no macroscopic system may oscillate indefinitely without consuming energy, so dissipation is not surprising *prima facie*. Yet, the maximum number of possible oscillations and the coherent quality of these oscillations remain unknown, until now. The first part of this work proves the upper-bounds on the number and quality of such oscillations when the system in question is homogeneously

[1] An obvious exception to this rule would be living biological systems. They are both nanoscale and have a large number of relevant states, but we try our best to focus on only the most essential parts.

driven and has discrete states. In a closed system, the maximum number of oscillations is bounded by the number of states. In open systems, the system size bounds the quality factor of oscillation, which is a figure of merit for the predictability of recurring behavior. This work also explores how the quality factor of macrostate oscillations, such as would be observed in chemical reactions, are bounded by the smallest loop in the reaction network, not the size of the entire system. The consequences of this limit are explored in the context of chemical clocks and limit cycles. This leads to the analysis of spontaneous oscillations in denatured GFPmut2, where, using these principles, we identify the oscillation mechanism to be the coordinated rearrangement of the hydrogen bond network of the β-barrel. We further calculate that the oscillations are touched off by one of the major loops adjoining the β-barrel, which provide a verifiable means to control the oscillation period.

To optically probe probing nanoscale systems of biological relevance with conventional techniques often requires one to use a focused laser to achieve highest possible signal contrast and resolution. Fluorescent labels in the sample absorb light from the laser and emit a photon with less energy. The detection of the low-energy photon then indicates the presence of the labeled object of interest. Unfortunately, the diffraction limit leads to a fundamental bound of the resolving power of the conventional microscope. To achieve higher resolution, we utilize nonlinear optics to probe the constituent structures of zebrafish muscle. In this case, nonlinearity is a tool for extracting additional information. Because the myosin fibers are asymmetric on the nanoscale, they have the ability to fuse two photons into one, a process known as sec-

ond harmonic generation. Instead of looking for a photon with less energy than the incoming laser, as with fluorescence, we try to detect photons with twice the energy of the incoming light. Second harmonic generation (SHG) based images can be very similar to fluorescence but with up to twice the resolution. Additionally, because light produced via second harmonic generation is coherent, while fluorescence is incoherent, the images have subtle yet significant differences, which we explore and explain. We use the wavelength dependence of the second harmonic generation conversion efficiency to extract information about the microscopic organization of muscle fibers, using the coherent nature of second harmonic generation as an analytical probe.

Second harmonic generation only occurs when the underlying material is asymmetric on the nanometer scale, and this is always the case at the boundary between two different materials. Existing experiments have used technique related to SHG, called sum-frequency generation (SFG), to directly probe the dynamics of free OH bonds at the water-vapor boundary. Using molecular dynamics simulations of the water surface, and by designating surface-sensitive free OH bonds on the water surface, we attempt to computationally reproduce the SFG experiment. The corresponding SFG susceptibility measurements were calculated and compared with those inferred from experiment. The method utilizes results available from independent IR and Raman experiments to obtain some of the needed quantities, rather than calculating them *ab initio*, allowing us to focus on the components of the water dynamics that best capture the observed SFG signature. We determine that the rotational dynamics, with a small quantum correction, are sufficient to produce the observed SFG signal.

The results provide insight into the microscopic dynamics at the air-water interface, and has useful application in the field of on-water catalysis.

To properly establish the path through all of these topics, I note my role in each. The first chapter is work which I have undertaken myself. The research on the GFPmut2 oscillations was directed by Rudy Marcus and advised by Scott Fraser, but the work is primarily my own. The work on zebrafish muscle was a close collaboration with Bill Dempsey, under the direction of Scott Fraser. Bill prepared all of the zebrafish for imaging, injected the morphants, and produced the transgenic fish. I imaged the fish and conducted the computations and theory. The SFG project was directed by Rudy Marcus, and it has since been published [1] and an addendum as been posted with necessary updates.[2] Yanting Wang produced the MD simulations. Yousung Jung and Professor Marcus spearheaded the project. I helped construct the theory with Professor Marcus and process the simulation data. Without this help and guidance from all of these individuals, especially Professors Marcus and Fraser, I certainly would not have much to report, nor would I know nearly as much as I do now.

[2] http://www.rsc.org/suppdata/cp/c0/c0cp02745f/addition.htm