Springer Theses
Recognizing Outstanding Ph.D. Research

Shashi Thutupalli

Towards Autonomous Soft Matter Systems

Experiments on Membranes and Active Emulsions

Springer

Springer Theses

Recognizing Outstanding Ph.D. Research

For further volumes:
http://www.springer.com/series/8790

Aims and Scope

The series "Springer Theses" brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student's supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today's younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

Shashi Thutupalli

Towards Autonomous Soft Matter Systems

Experiments on Membranes and Active Emulsions

Doctoral Thesis accepted by
the University of Göttingen, Germany

Springer

Author
Dr. Shashi Thutupalli
Department of Physics
Princeton University
Princeton, NJ
USA

Supervisor
Prof. Stephan Herminghaus
Department for Dynamics of Complex Fluids
Max Planck Institute for Dynamics and Self-Organization
Göttingen
Germany

ISSN 2190-5053 ISSN 2190-5061 (electronic)
ISBN 978-3-319-00734-2 ISBN 978-3-319-00735-9 (eBook)
DOI 10.1007/978-3-319-00735-9
Springer Cham Heidelberg New York Dordrecht London

Library of Congress Control Number: 2013943706

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

To my parents and grandparents

Supervisor's Foreword

The spontaneous formation of patterns and structures in systems far from thermal equilibrium belongs to the most fascinating phenomena in nature. Without such processes there would not be any life, leave alone anyone to do science. The bizarre morphologies into which bacterial colonies evolve, the dazzling number of interdependent self-organizing sub-systems (ions, nucleic acids, proteins, organelles) which organize their metabolism, yield just a glance at the immense organizational power of living systems. Yet the overarching principles of such self-organizing, autonomous systems are as yet elusive.

In order to achieve a deeper understanding of the underlying physics of self-organization, and possibly to venture out into new areas of application, it would be very desirable to come up with artificial systems which imitate life at the microscopic level. In fact, recent developments in droplet-based microfluidics have paved the way to the preparation of compartmentalized soft-matter systems consisting of similar building blocks as cellular organisms.

The work Shashi Thutupalli is presenting here provides a considerable step forward in this direction. Rafts of droplets of aqueous suspensions are created which are separated from each other only by lipid bilayers. It is shown that the latter can not only be used to incorporate membrane proteins such as ion channels, but also as interesting nonlinear electrical circuitry elements. By introducing oscillating chemical reactions in the droplets, complex coupling patterns can be observed which depend upon the properties of the membranes between adjacent droplets. This provides already a high-level integration of nonlinearity, pattern formation, and biological building blocks.

In a further step, the packing density of the droplets is reduced such that they become freely mobile. A formulation is found which gives rise to locomotion of the droplets, such that their collective behavior can be investigated as another direct consequence of nonequilibrium physics. By a simple rectification experiment, it is demonstrated that the behavior of swarming droplets is fundamentally different from diffusing Brownian particles, although it appears similar to the unexperienced eye. Other striking phenomena like single-file diffusion of active particles can be studied here as well.

In a nutshell, this book provides deep insight into self-assembly and collective phenomena in systems which are extremely versatile and can be well controlled. It is to be expected that it will spur a considerable amount of further research into autonomous soft-matter systems.

Göttingen, May 2013 Prof. Stephan Herminghaus

Acknowledgments

I owe my deepest gratitude to Prof. Stephan Herminghaus for his supervision and guidance during this work. He has provided me with innumerable opportunities, has let me fly with my imagination when I wanted to and has led me by hand when I needed it. I still remember my first meeting with him at the DB Lounge in the Frankfurt train station and it has, since, been a most delightful and significant journey in my life. Stephan's infectious scientific temper, the way he thinks about scientific questions and the wonderfully stimulating atmosphere he creates in the department will remain indelible influences throughout my life. For all the discussions, motivation, for your support and understanding during the hurried thesis writing, for that unforgettable retreat on the sailing boat, and above all, for being a Doktorvater in the truest sense of the word, thank you Stephan!

Prof. Dr. Ralf Seemann has played an invaluable role in my Ph.D. journey. As part of his group I always enjoyed and benefited from the discussions during the group meetings. Together with Prof. Karin Jacobs, he organized winter schools at Feldberg, that were a fun part of my Ph.D. tradition. For your support and guidance, in spite of being in far away Saarbrücken, and in fact at all times, I am very grateful to you Ralf.

My thesis committee members, Prof. Dr. Christoph Schmidt and Prof. Dr. Eberhard Bodenschatz have provided me great feedback about my work. I fondly remember the week at Il Ciocco where I had a great chance to spend considerable time with Prof. Bodenschatz. His feedback about my work and his kind words of advice about my career came at a very timely moment.

I was very fortunate to be a part of the SFB 755 that was led by Prof. Dr. Tim Salditt. I thank him for his enthusiastic organization and discussion during the winter and autumn schools of the SFB where I learnt a lot of new things and many new scientific questions opened up for me. More importantly, I thank him and Dr. Andre Beerlink for the collaboration on the phase contrast imaging project. Tim and I were the 'day time team' at the ESRF during one intense week of measurements and needless to say I learnt a lot working with him. Matthias Bartels and Michael Mell were the remaining members of that collaboration to whom I am very grateful. It was always interesting to work together with Andre on that project and I wish him very well in his career and look forward to a similar successful collaboration in the future.

I met Dr. Geert van den Bogaart at a 2-day methods course that he organized and those 2 days led to 'side project' that lasted many Friday afternoons over 2 years. We did some exciting experiments together, had many great discussions about membrane fusion and life in general and it was always fun! It was a serendipitously wonderful collaboration and has formed a crucial part of my thesis.

I met Dr. Sergio Alonso at the DPG meeting in Regensburg and he ended up doing some beautiful simulations of B–Z droplets. I really look forward to completing that story with him very soon. Sergio was a terrific host to me at Berlin and I look forward to seeing him again soon! Prof. Marcus Hauser has been very encouraging of my work and provided me with a very kind invitation to visit his group at Magdeburg. It was enriching to talk to him about all things BZ and he showed me the delightful world of the plasmodium, where a lot of promise lies. I thank Prof. Holger Stark, Dr. Vasily Zaburdaev, Andreas Zöttl and Max Schmitt, who hosted me in Berlin, and for their inspiring discussions about squirmers. At the very beginning of my thesis, Dr. Jakob Sorensen and Jens Weber at the MPIbpc showed me how to make measurements with a patch clamp amplifier—later, I had many hours of fun, playing with the amplifier!

Monika Teuteberg is a wonderful colleague! Without her help and patience, many things will simply not be possible at the department. My mornings started with her cheery greeting as I walked past her office. It is not the same anymore at the Bunsenstrasse, Monika! Antje Erdmann and Michaela Böttcher have been very kind, efficient and helped me immensely with all the GGNB administration. I thank Udo Krafft and Wolf Keiderling for their technical help during this work. Thomas Eggers, Kris Hantke, and Sibylle Nägle kept the computers and printers and networks running smoothly, with only the finest paper jams.

I have great colleagues and many of them have become good friends, helped us with adjusting to life in Germany and made us feel at home here—Konstantina, Semra, Krish, Venkat, Enkhtuul, Mario, Zeina, Audrey, Shuang, JB, Ciro, Julie, Martin, Jürgen, Thomas, Matthias, Jean-Christophe, Quentin, Sandro, Sonia, Christoph, Max, Jean-Francois, Katherine, Klaus, Siddharth, Pramod, Daniel, Johannes, Marta, Ohle. I especially thank Eric for sharing the 'madness', like only he and I will understand. Thank you all very much for enriching my Ph.D. days. I hope that our paths will cross in the future!

Away from work, many friends have made my time in Göttingen unforgettable. I had many lively weekends and evenings with them. Krish, Venkat, Harish, Shweta, Vimal, and Atul were the first people I met and will remain in my heart always. Spending time with Srinivas was always engaging—I will never forget our violin playing times. Gopal, Soujanya, Swathi, Mayur, Eshwar, Aniket, Sarath, Varun, Sai, Karthik, Bhaskar, Sonia, Anjali, Durga, Raj, Anmol, Ratika, Sridhar, Raunak, and many many more, whose faces I remember but names have faded away, have made it especially memorable for me.

My friends Rajiv Iyer, Umakant Rapol, Kunj Tandon, Ayan Bannerjee, and Shankar Chandrasekharan motivated me greatly toward doing a Ph.D. Guys, here it is. Thank you very much!

Simply put, nothing would be possible or even meaningful without my family. My parents, amma and naanna, have been my strength. Their love, care, and prayers have made me what I am and anything I do in my life will always be because of them. My grandparents have been my guiding spirit throughout my life—not a day goes by that I do not think about them fondly. My in-laws, attayya and mamayya, akka, Mintu, Seenu, Lien, and all the kids have supported me with everything and their love is wonderful. And Sravanti. Any amount of words I write for her will fall woefully short of all that I feel. She has been a constant source of succor, love, strength, and pure joy. The Ph.D. work and this thesis would not be possible without her. I think it suffices to say that she complements me in every way imaginable. Sravanti, it's always you and I. Thank you!

Abstract

This book presents experiments on lipid bilayer membranes and nonequilibrium phenomena in active emulsion droplets. In the first part, we outline a concept of self-assembled soft-matter devices based on microfluidics, which use surfactant bilayer membranes as their main building blocks. Membranes form spontaneously when suitable water-in-oil emulsions are forced into microfluidic channels at high-dispersed phase volume fractions and are remarkably stable even when pumped through the microfluidic channel system. Their geometric arrangement is self-assembling, driven by interfacial energy and wetting forces. The ordered membrane arrays thus emerging can be used to build wet electronic circuitry, with the aqueous droplets as the 'solder points'. Furthermore, the membranes can serve as well-controlled coupling media between chemical processes taking place in adjacent droplets as is shown for the well-known Belousov–Zhabotinsky reaction. We also investigate the dynamics of the fusion of vesicles with bilayer membranes. The particular process that we study is the fusion mediated by the SNARE-proteins embedded in the membranes. It is shown that the electrostatic repulsion between the membranes, due to the charged lipids that comprise them, blocks their fusion. Under such conditions, the conformational change of the membrane protein Synaptotagmin-1, under the influence of Ca^{2+} binding, restores membrane fusion. Thus we show in vitro, for the first time, the massive increase in the membrane fusion due to Ca^{2+} triggering, as is the case in vivo. Further, we present a propagation-based X-ray phase contrast imaging to study structure and interfacial properties of ultrathin model membrane systems.

A scheme of active self-propelled liquid microdroplets which closely mimics the locomotion of some protozoal organisms, so-called squirmers, is presented. In contrast to other schemes proposed earlier, it is demonstrated that locomotion paths of the swimmers are not self-avoiding, since the effect of the squirmer on the surrounding medium is weak. Our results suggest that not only the velocity, but also the mode of operation (i.e., the spherical harmonics of the flow field) can be controlled by appropriate variation of parameters. We have studied experimentally the collective behavior of such self-propelling liquid droplets. We find strong polar correlation of the locomotion velocities of neighboring droplets, which point to the formation of ordered rafts. This shows that pronounced textures, beyond what has been seen in simulations so far, may show up in crowds of simple model squirmers, despite the simplicity of their (purely physical) mutual interaction. As such, the self-propelled droplets are not restricted by the classical equilibrium constraints such as the fluctuation dissipation theorem. We build a correlation ratchet, which relies on a broken detailed balance, to demonstrate a passive rectification scheme of a population of the swimmers. Finally, we study the collective dynamics of a population of swimmers when they are confined to a single dimension, in a setting similar to the well-studied single-file diffusion. It is shown that when the short-time dynamics of the swimmer are ballistic, a transition to a diffusive behavior is seen at the long times and when the short-time dynamics are diffusive, the long-time dynamics follow an anomalous diffusion law, as predicted by theory.

Contents