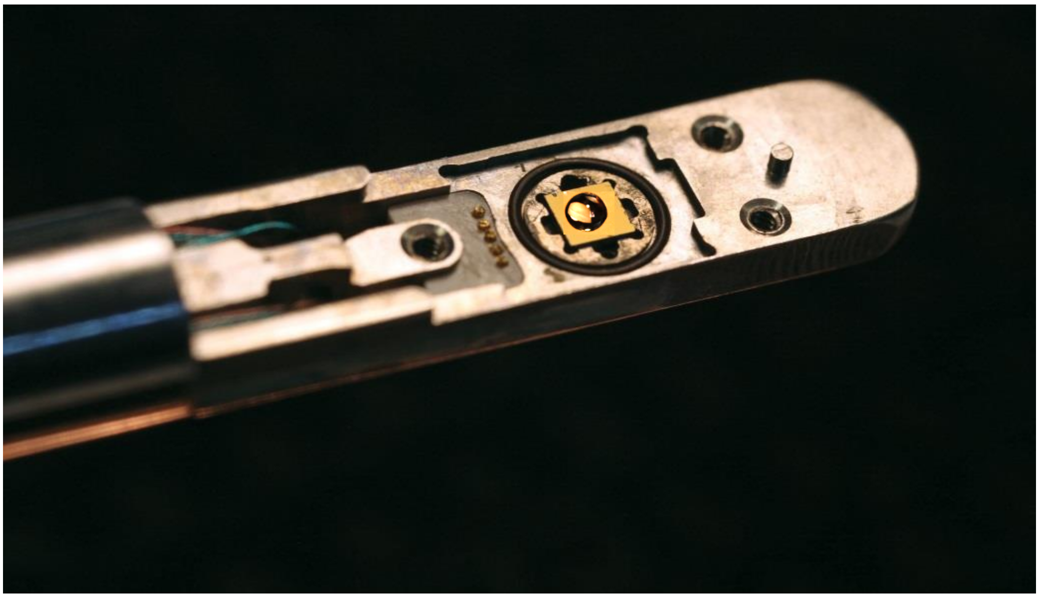
Electron holography and particle dynamics in liquid phase transmission electron microscopy

Murat Nulati Yesibolati
PhD Thesis March 2018

DTU Nanotech
Department of Micro- and Nanotechnology

Ph.D. Thesis

Electron holography and particle dynamics in liquid phase transmission electron microscopy



Murat Nulati Yesibolati

Department of micro- and nanotechnology
Technical University of Denmark

March 2018

DTU Nanotech
Department of Micro- and Nanotechnology

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Technical University of Denmark (DTU). The research project was funded by DTU and partial support from the Danish Research Council for Technology (Production Case No. 12-126194). The research was conducted in the Molecular Windows research group, Department of Micro- and Nanotechnology (DTU Nanotech) from March 15th, 2015 to March 14th, 2018.

Thesis title

Electron holography and particle dynamics in liquid phase transmission electron microscopy

---

Supervisor Committee
Main Supervisor: Kristian Mølhave, Associate Professor, DTU nanotech
Co-supervisor: Takeshi Kasama, Senior Researcher, DTU CEN
Co-supervisor: Hongyu Sun, Postdoc, DTU nanotech

Assessment committee
Jakob Birkedal Wagner, Professor, Center for Electron Nanoscopy DTU, Denmark
Rafal E. Dunin-Borkowski, Professor, Research Centre Jülich, Germany
Utkur M. Mirsaidov, Assistant Professor, National University of Singapore, Singapore

Cover illustration
A custom made liquid electrochemical TEM holder
By Murat Nulati Yesibolati
Photograph by Jesper Scheel, Graphic Designer DTU nanotech

Ph.D. Thesis
By Murat Nulati Yesibolati
Department of micro- and nanotechnology. DTU nanotech
Technical University of Denmark

Abstract

Liquid phase transmission electron microscopy (LPTEM) enables us to visualize structures and the evolution of processes directly within liquid environments, with high spatial and temporal resolution. As such, LPTEM can shed light on both fundamental questions in physics, materials science, chemistry, soft matter and bioscience. In this thesis, an LPTEM platform was developed, based on silicon nitride membrane encapsulation of the liquid sample. This thesis explores three questions leading to new ways to perform LPTEM and providing new types of information on fundamental processes:

- Is it possible to perform LPTEM studies of freely diffusing particles' dynamics?
  Detailed LPTEM observations were made of free Brownian motion of nanoparticles in liquids, where all previous studies have focused on the far slower particles that are strongly interacting with the membranes. We measure to what extent it is influenced by the electron beam and discuss how this may be used for new LPTEM studies that may better model bulk liquid behavior than particles trapped on the membrane.

- Can electron holography be used to measure electrical potentials in liquids?
  Electron holography has been widely used in mapping electromagnetic fields in solid matter, and if electron holography can be reliably applied in LPTEM it could lead to better understanding of the driving forces in electrochemistry, imaging magnetic interactions etc.
  Quantitative liquid phase electron holography is demonstrated in LPTEM using a newly developed nanochannel liquid cell. The mean inner potential (MIP, V_0) of liquid water is measured to be $V_{0,H2O} = 4.48 \pm 0.19$ V, which is comparable to revised quantum mechanical model calculations. The consistency between the quantum mechanical MIP and experimental MIP is an essential benchmark to improve the quantum mechanical models that help us understand water interactions in liquid processes.

- Can we measure local charge distributions of nanostructures in liquid by using electron holography?
  Mapping charge distributions on nanostructures in the liquid phase would provide a new approach to understanding the important electrostatic interactions in liquids. Electron holographic analysis was used to explore the possibility to quantify the charge distributions in LPTEM systems and on individual nanoparticles immersed in liquid.

This thesis takes the first initial steps in developing LPTEM holography, and find it is a promising method that likely will open up many fascinating possibilities to study electromagnetic interactions at the nanoscale in liquids, and hence lead to new insights in nanoscale dynamics.

Resumé (Danish)

Væske-fase transmission elektron mikroskopi (LPTEM) gør det muligt at observere strukturer og udviklingen af processer direkte i væsker med høj opløsning i rum og tid. LPTEM kan derfor hjælpe med at give ny information om grundlæggende spørgsmål inden for fysik, materialer, kemi, og biologiske strukturer og processer. I dette projekt blev der udviklet en LPTEM platform, baseret på siliciumnitrid membran til at indkapsle væskeprøven. Afhandlingen udforsker tre spørgsmål som leder til nye LPTEM metoder der kan give helt ny information om grundlæggende processer i væsker:

- Er det muligt at lave LPTEM studier af partikler i fri diffusion?
  Detaljerede LPTEM målinger blev lavet på nanopartiklers frie Brownske bevægelser i væsker, hvor alle tidligere studier har fokuseret på langt langsommere partikler stærkt interagerende med membranerne i systemet. Vi har målt hvor meget elektron strålen påvirker processen og diskuteret hvordan dette kan blive brugt i nye LPTEM studier der bedre ville kunne imitere relevante betingelser af væske end det er muligt med partikler tæt på membranen.

- Kan elektron holografi bruges til at måle elektriske potentialer i væsker?
  Elektron holografi er blevet bredt brugt til at kortlægge elektromagnetiske felter i faste stoffer og hvis metoden kan bruges i LPTEM ville det kunne give bedre forståelse af drivkræfterne i elektrokemiske grænseflader og vekselvirkninger mellem partikler osv.. Kvantitativ elektron holografi blev brugt sammen med et nyligt udviklet nanokanal LPTEM system til at måle det gennemsnitlige elektriske potentiale i vand (mean inner potential, MIP) V0,H2O = 4.48 ± 0.19 V. Værdien er sammenlignelig med opdaterede kvantemekaniske modelberegninger og er et vigtigt grundlag for at sikre gode modeller der bidrager til bedre forståelse for mange processer i vand.

- Kan vi måle ladningsfordelinger på nanostrukturer med elektron holografi?
  Hvis vi kan kortlægge ladningsfordelinger i væsker vil det give en helt ny tilgang til at forstå grundlæggende elektrostatiske drivkræfter i mange processer I vand. Elektron holografi blev brugt til at undersøge om det er muligt at kvantificere ladningsfordeling i LPTEM systemer og på individuelle nanopartikler i væsker.

Denne afhandling tager på denne måde de første skridt til at udvikle LPTEM holografi og viser at det er en fascinerende metode der sandsynligvis kan åbne nye muligheder for at forstå elektromagnetiske vekselvirkninger i væsker. Dette kan give fornyet forståelse for nanoskala processer og dynamik i væsker.

Scientific contributions

Papers in preparation for peer review publication

M. N.Yesibolati, H.Y. Sun, K.I. Mortensen, S.Tidemand-Lichtenberg, A.B. Bluhme, K. Mølhave, “Faster-Than-Bulk Brownian Motion of Individual Nanoparticles Induced and Measured by Liquid Phase Scanning Transmission Electron Microscopy”, **Manuscript in preparation, refer to Chapter 5**

M. N.Yesibolati, S. Laganà, H.Y. Sun, , M. Beleggia, S. M. Kathmann, T. Kasama, K. Mølhave, “Electron Holographic Benchmark for Quantum Models of Liquid Water”, **Manuscript in preparation, refer to Chapter 6**

M. N. Yesibolati, H.Y. Sun, S. Lagana, S. Canepa, S. M. Kathmann, T. Kasama, M. Beleggia, K. Mølhave, “Mapping charges of nanoparticles in liquids using off-axis electron holography”, **Manuscript in preparation, refer to Chapter 7**

Peer reviewed publication

M.N. Yesibolati, S. Laganà, T. Kasama, H.Y. Sun, K. Mølhave, “Using nanochannel microfluidic chips for measuring the mean inner potential of liquid water”, ***Microscopy and microanalysis*,** 22 (2016) 86-87

As coauthor

S.Laganá, E.K. Mikkelsen, **M.N. Yesibolati**, H. Sun, T. Kasama, O. Hansen and K. Mølhave, “Energy Filtered Transmission Electron Microscopy measurement of the Inelastic mean free path in water using a Novel Nanofluidic Liquid Cell”, **Under submission**

S. A. Canepa, **M.N. Yesibolati**, H.Y. Sun, K. Mølhave, “Direct Observation of Anisotropic Nanoscale Galvanic Replacement Reactions towards Mechanistic Understanding: Liquid Cell Scanning Transmission Electron Microscopy Studies” **Under submission**

S. A. Canepa, **M. N. Yesibolati**, C. Nielsen, H.y. Sun, H. Bruus, K. Mølhave, “Systematic study of electrochemical dendritic growth and morphological evolution by in situ liquid cell scanning electron microscopy” **Manuscript in preparation**

J. Zhao, L.B. Sun, S. Canepa, H.Y. Sun, **M.N. Yesibolati**, K. Mølhave, Z.C. Xu, “Phosphate tuned copper electrodeposition and promoted formic acid selectivity for carbon dioxide reduction”, ***J. Mater. Chem. A***, 5 (2017) 11905-11916

Conferences

M.N. Yesibolati, Simone Laganà, Takeshi Kasama, Hongyu Sun, Kristian Mølhave, “Using nanochannel microfluidic chips for measuring the mean inner potential of liquid water”, 3rd International Conference on In-Situ and Correlative Electron Microscopy, **October 2016, Germany**

M. N. Yesibolati, Silvia Canepa, Rolf Møller-Nilsen, Simone Laganà, Hongyu Sun, Kristian Mølhave, "Developing methods for In-situ TEM and correlated electrochemistry studies" The XIVth International Conference on Electrified Interfaces, **July 2016, Singapore**

M. N. Yesibolati, Mølhave, Kristian, "Developing methods for In-situ TEM and potential studies in energy storage, electrochemistry, material science, and bioscience" Sustain DTU conference, **December 2015, Denmark**

Membrane-based electron microscopy platforms

A membrane-based liquid electrochemical TEM holder (**Chapter 2, Figure 2.5**)
M. N. Yesibolati, S. A. Canepa, R.E. Møller-Nilsen, H.Y. Sun, K. Mølhave

A membrane-based liquid TEM holder (**Chapter 3, Figure 3.4**)
M. N. Yesibolati, S. A. Canepa, R.E. Møller-Nilsen, H.Y. Sun, K. Mølhave

A membrane-based liquid electrochemical SEM platform (ECSEM)
M. N. Yesibolati, S. A. Canepa, R.E. Møller-Nilsen, K. Mølhave (**Appendix I**)

A membrane based biprism holder
M.N.Yesibolati, J. Ærøe Hyllested, W. Huyzer, T. Kasama

Additional information

Two different liquid cells have been used in this thesis: the sandwiched liquid cell and the nanochannel liquid cell. Both cels have their own featured TEM sample holders and chips. I have engineered both TEM holders, designed and partially participated in microfabrication of the sandwiched liquid cell chip together with Dr. Silvia Canepa. The nanochannel liquid cell chips were designed and fabricated by Dr. Simone Laganà.

List of abbreviations and symbols

TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
LP(S)TEM	Liquid Phase (Scanning)Transmission Electron Microscopy
FEG	Field Emission Gun
BF	Bright Field
DF	Dark Field
ADF	Annular Dark Field
HAADF	High Angle Annular Dark Field
FOV	Field of View
CCD	Charged Coupled Device
FFT	Fast Fourier Transform
IAM	Independent Atom Model
UHV	Ultra-High Vacuum
SiN_x	Silicon rich nitride
Si_3N_4	Stoichiometric silicon nitride
CVD	Chemical Vapor Deposition
MSD	Mean Square Displacement
CVE	Covariance-based Estimator
SD	Standard Deviation

λ	Wave length or Inelastic mean free path
t	thickness
ψ	Electron wave
β	Electron source brightness
I	Image intensity
A	Image amplitude
μ	Fringe contrast
q_c	Fringe carrier frequency
W	Fringe width
φ	Image phase
σ_φ	Phase sensitivity
h	Planck constant
V_0	Mean inner potential (MIP)
$\rho(r)$	Charge distribution
Ω	Cell volume
D	Diffusion coefficient
η	Viscosity
k_B	Boltzmann constant
∇^2	Laplacian operator
ε_0	Vacuum permittivity

Acknowledgement

First and foremost, I would like to thank my advisor Kristian Mølhave. I appreciate your contribution of funding, ideas, time to make my PhD research experience productive and stimulating. Thank you for your constant patience and encouragement. I never hesitated to walk into your office to ask questions and suggestions. Thank you for all the critical comments in shaping my research work and the thesis chapters! I have learned a lot from you about how to do interesting and challenging scientific research. I cannot thank you enough! I would also like to thank Hongyu Sun. Your expertise in TEM made our research much easier. I enjoyed working with you and the friendship! My thanks also go to Takeshi Kasama. Thank you for your guidelines in electron holography. Half of the project is turned out to be liquid phase electron holography, and I could not make it without your continued help and support. Also, I would like to express my thanks to Dr. Marco Beleggia, Dr. Kim Mortensen. Dr. Shawn M. Kathmann. I appreciate your time, thoughtful discussion and inputs in different parts of my PhD project.

I would like to thank my groupmates and friends. Silvia, I always enjoyed the time we spent together. You know how challenging the project is. Simone, the nanochannel liquid cell you fabricated made almost half of my PhD project possible. Lots of credits to you! Anders, we enjoyed drinking beers together, and thanks for the laughs and coffee every time when you were in DTU office. You are chemist who can code. I appreciate your help in analyzing data in diffusion work. Rolf, despite your busy time during your last PhD year, I still learned a lot from you about liquid electron microscopy. You are the guy who knows what works and why it works. Thanks for correcting my thesis!

This PhD project is nearly impossible without support from DTU CEN and Danchip. Willie, I appreciate that you and CEN allow me fabricating custom-made holders and run liquid experiment in the precious TEMs. Adam and Berit, thanks for your help in SEM. Luckily, we did not blow up the Inspect “very often” with liquid! Thank you Zoli, Jens, Thomas, Lili, Pei, Monia, Jes, Jacob and Jeppe for help in CEN; Louise, Helle, Karen in the cleanroom; Jeppe in the electronic workshop. Thank you Majken, I learned a lot how to keep a safe research lab.

Many thanks also go to colleagues and friends in Nanotech. Per, thanks for many help in workshop. Tim and Joachim, thanks for your patience and we will do some fun science together after the PhD. Jon and Anders thanks for the free beers always. Lucia, Chantal, Maria, it is fun and relax talking with you three. Lene and Mathias, I know I always get covered in the party. Chen, Bingdong, Xin thanks for help in cleanroom work and talks at late 9pm. Thanks Suhith, Siyin, Solène, Ritika, Dirch, Joachim, Johanna, Hoà, Jing, Feng, Abhay, Onur, Kuldeep, for the fun time spent together in our apartment and yours. Louise, Tine, Dorthe thanks for all the administrative help and it saved me lots of time. Thank you Sarah for keeping our lab safe and clean. Thank you Jesper, there are some photos in this thesis go to your credit.

There are some friends also deserve special thanks. Abu, Azmat, Rehima, Ai, Muhtar, Rena and Bilge. You made my life in Denmark much easier. Abu, your determined and insightful thoughts calmed me down many times and thanks for the good food. Azmat,

thanks for the time playing together, especially at the end of the PhD which also helped me escape from continuous writing once a week. Also thanks for my friend Liang, Mirela, Arash, and the dogs Chuggy and Hugo at home, I feel relaxed with you after a long day work and writing.

At the end, Dad, thank you for the jokes and teasing words. I always feel grateful that we could talk like friends. Your attitudes towards life become a driving force in my life too. Mom, thanks for being serious about everything and always planning ahead, which Dad and I always tried to learn but failed most of the time. All the families' stories heard from you always made me laugh. My sisters and brothers in law, S'ynar, Aidyn, Tan'nur, Duman, thanks for your understanding and being supportive in the last three years. My nephews and nieces, Sai'at, Eren, Eli'na, Rai'ana, it was so much fun with you every time when I was home.

12.03.2018
End!

Table of Content

Published by:
DTU Nanotech
Department of Micro- and Nanotechnology
Technical University of Denmark
Ørsteds Plads, building 345C
DK-2800 Kgs. Lyngby