A Bubble Is Born: Nucleation and Early Growth of CO2 Bubbles in Polymer Foams

Thesis by
Andrew Samuel Ylitalo

In Partial Fulfillment of the Requirements for the
Degree of
Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California

2022
Defended Friday, May 20, 2022

© 2022

Andrew Samuel Ylitalo
ORCID: 0000-0003-4086-3508

Some rights reserved. This thesis is distributed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License
Scripture quotations marked (NIV) are taken from the Holy Bible, New International Version®, NIV®. Copyright © 1973, 1978, 1984, 2011 by Biblica, Inc.™ Used by permission of Zondervan. All rights reserved worldwide. www.zondervan.com The "NIV" and "New International Version" are trademarks registered in the United States Patent and Trademark Office by Biblica, Inc.™

Acknowledgments

Why do we acknowledge the support of others? To be kind? To ingratiate ourselves to others? To remind ourselves that the role we play in our own work is a humble fraction of the collective effort that makes it possible? Maybe.

Here, I acknowledge those who helped me so my readers and I can pause to remember that life can, as God declared on the sixth day, "indeed [be] very good."[1] Of course, life can also be not very good. Without those moments of difficulty, despair, and disillusionment, however, I would not have grown into who I am today, for "we also glory in our sufferings, because we know that suffering produces perseverance; perseverance, character; and character, hope."[2] That I grew from those moments instead of receding, emerged hopeful instead of jaded, and look back with joy and not disgust is thanks to all of you.

First, thank you, Julie. I did not know what I sought from my PhD, but I believed that your curiosity, humility, hope, and integrity would lead me to something good; indeed, they did. I aspire to live up to the example you set. And while I regret dismissing your detailed questions that challenged my ideas at first, I know now that those are the questions that shall forever echo in my head, guiding me ever closer to Truth. Zhen-Gang, I have never met anyone who expects such excellence, communicates with such clarity, and seeks understanding with such earnestness as you. I am especially thankful to have seen the meaning of clarity and pedagogy embodied in your lectures and for your encouragement and academic support to pursue my interest in complex coacervation.

I thank the rest of my committee, Profs. Rustem Ismagilov, Richard Flagan, Mitchio Okumura, and John Brady, for taking the time to review my work and advise me on next steps. Rustem, you have taught me how to defend my ideas with professionalism. Rick, you have led me in directions I never would have pursued and that now form an integral part of my thesis. Mitchio, thank you for your kind support. John, thank you for letting me do my demo of beverage foam in class. Thank you also for not letting go of the importance of radial convection—it turned out to be quite important.

I first want to thank my first and forever research advisor, Prof. Andre

[1] Book of Genesis, Chapter 1, verse 31, King James Version

[2] St. Paul's Letter to the Romans, ch. 5, v. 3–4, New International Version

Mkhoyan of the University of Minnesota, whose encouragement, recommendation, and guidance brought me to Stanford and then Caltech, and finally to the completion of my PhD. Everyone needs a mentor like Andre. I would also like to thank Prof. Gerry Fuller, my undergrad advisor, for practically twisting my arm to join his lab in 2015, where I grew to love fluid flow, imaging, and image processing that prepared me for this project at Caltech. Last, I thank Prof. John Frostad for mentoring me throughout the Fuller lab and beyond, and for teaching me the simple tenacity of trying things out and seeing what happens. My confidence in myself as a researcher and a programmer is largely due to your years of mentorship.

Thank you to the teams I've worked with at Dow, in person, and remotely: Dr. Tom Fitzgibbons, Dr. Weijun Zhou, Dr. Valeriy Ginzburg, Dr. James Griffith, Dr. Bill Winniford, Dr. Paul Gilles, Marla Gilbert, Dr. Steve Horvath, Dr. Irfan Khan, and Dr. Jacob Crosthwaite. Thank you for investing in the success of this project and supporting my ideas since before I came to Caltech. Yours was my first collaboration, and it set an excellent example for those to come. Grazie assai a Prof. Ernesto Di Maio per ospitarmi nel suo laboratorio per l'estate, e anche ai miei amici napoletani, Vincenzo Il Grande, Vincenzo Il Piccolo, Fabrizio, Antonio, Pepe Scherillo, e Valerio per qualche panini, pizze, tazze di caffè, e conversazioni indimenticabili durante l'ora di pranzo ogni giorno. Mi vita è cambiata nel senso migliore grazie a Napoli e la sua gente imparagonabile.[3] Thank you to Lison, Fulvia, Pepe, Giovanni, Riccardo, and Huidong for making those eternal and error-prone nights in the Death Star (Argonne) bright with laughter and smiles; special thank you to Lison for your persistence in turning the data from those nights into a story worth publishing.

Without the National Science Foundation's Graduate Research Fellowship Proposal and the Dow University Partnership Initiative, this work would not have happened. While the funding provides potential, it is the people who realize it: thank you Tom and Weijun for your consistent feedback throughout my entire PhD and the mentorship you provided as I looked to my next steps. Thank you especially for supporting my research excursions in Naples, Italy, and Lake Jackson, TX, which transformed both the academic and personal experience of my PhD. Thank you also to the Armenian Professional Society for the scholarship that supported the costs of

[3] "Thank you very much to Prof. Ernesto Di Maio for hosting me in his lab for the summer, and also to my Neapolitan friends, Vincenzo the Great, Vincenzo the Small, Fabrizio, Antonio, Pepe Scherillo, and Valerio for some unforgettable sandwiches, pizzas, espressos, and conversations during the lunch hour every day. My life has changed in the best way thanks to Naples and its incomparable people." (Italian)

these excursions. Thank you to the cheerful, professional, and supportive staff I had the pleasure to work with: Christine Jary, Abigail McCann, Kate, Allison Kinard, and Kathy Bubash. Thank you Prof. Giapis for taking me on as a TA despite my incomplete chemical engineering background, as well as for the sushi afterward.

Thank you Kriti Chaturvedi for teaching me about the effects of flow on bubbles through her OpenFOAM simulations. Thank you Dr. Justin Bois for teaching me how to manage my data in my first months at Caltech. I would have had no hope of deciphering my past work while writing this thesis were it not for the practices you instilled in me and enthusiasm for clean data analysis in your class. Thank you Dr. Huikuan Chao for not only building the strong platform of theory and modeling on which this thesis was built, but for the time you dedicated to teaching a novice like me not only how to use it, but how to understand it and teach it to others. My academic journey as a theorist began with you.

Thank you Sameer and Harsha for making the upper floor of Steuben a home and the lower floor home to many fond memories of movie nights and dinner over *Rick and Morty*. Thank you Tega for showing me that I can still be fascinated by physics and math as an engineer. Thank you Christoph for teaching me how to fix the bugs in my installation of OpenCV and other C++ problems that had been holding up my image-processing analysis. Grazie mille a Tiziana Di Luccio e la sua famiglia carina, per chi ho un sacco di d'amore.[4] Gracias a Tony por ser un amigo paciente, cómico, y generoso.[5] Gracias también a Leslie por darme un descanso del trabajo con sus historias animadas y por no tener miedo delante de la muerte—todo antes de las 9 en la mañana.[6] Thanks to Brian Wilson for doing a won-won-won-wonderful job making me SMiLE. Thank you immensely to Isaac Swanlund, who turned an aimless walk in the wilderness into a coding project that saved me literally hundreds of hours processing data and taught me enough about programming in teams to get a job. Your impact on my life is understated yet ever-present.

[4] "Thanks a thousand to Tiziana Di Luccio and her lovely family, for whom I have lots of love." (Italian)

[5] "Thank you, Tony, for being a patient, funny, and generous friend." (Spanish)

[6] "Thank you also to Leslie for giving me a break from work with your animated stories and for having no fear before death—all before 9:00 a.m." (Spanish)

شكرًا يَا سَامي لصدَاقتك. أَنَا دَرَستُ العَربية كثيرًا منك.[7]

Huge thank you to the Luys Mens Club (Shaunt, Armen, and Hopar Varag) for good living without hesitation, tossing out nuggets of life wisdom, and giving me an excuse to get good kebab.

Thanks Kyle and Camila for bringing a bit of the vibrancy of our life at Stanford here with us to Pasadena. Deanna, Alice, Scott, Nilo, and Alyssa for being the best physics friends a physicist could have. Mike, Gerardo, Teun, Tamu, and Tynan for reminding me of good times. Mike especially for treating me like an expert and a scientist when I lost sight of what I had to offer academically. Danny for keeping in touch.

Erik. Twenty-seven years says it all. Graham for your indomitable and infectious fascination with science and engineering of all types—nobody else listens with such interest when I ramble about my PhD. Shelby and Nick, Will, Jordan and Yeongseo, Emily and Joe, Lauren and JJ, Toby, Kelsee, Clare, and Chi (who visited twice!) for being Stillwater's finest twenty-some seasons straight.

Mr. Symalla for teaching me about experimental research. Though you told us many times, I doubted that the fourth-quarter project had that much to do with getting a PhD. I was wrong. Thank you for bringing in those two grad students, too. I have often thought back to how they said that the PhD requires you to think about your problem constantly. That scared me at first, but I have come to find joy in this engrossment of late. Mrs. G., the greatest teacher I never had. You were a true friend and support during the first years of my PhD, always ready to catch up and keep in touch. I treasure your creative postcards. Mr. Lindsay, where would my ducks be if not for you? Definitely not in a row—that's for sure.

Thank you Paresh for your eagerness to share your boundless knowledge and earnest wisdom; you have been a great support in both the best and worst times and gave me confidence during my job search with your relentless optimism. Thank you, also, for reading my drafts of this thesis so thoroughly and offering thoughtful comments. Thank you Orland for being my first mentor at Caltech and getting this project off the ground when I was still afraid of the laser cutter. Thank you Rachel for being a great office mate, sounding board, and happy answerer of questions, as well as a great friend. Thank you Red for the most sincere and attentive responses to any question and request for help I ask of you. Thank you Rob for talking shop and

[7] "Thank you Sammy for your friendship. I learned a lot of Arabic from you." (Arabic)

making the lab a fun place. Thank you Lealia for your creative suggestions on how to make my presentations pop (and for generally having beautiful presentations) and for making the lab run more like a lab should run. Thank you Jin for fun chats after long days in the lab and making biology understandable to me. Thank you Ben for always having time to help and an eagerness to invest in teaching me the deeper lessons you took from your time at Caltech. You've been a good collaborator and a delightful friend. Thank you Alex for reminding me every day how exciting it is to explore cool science and how to be fearlessly curious. Thank you Hojin for help keeping the lab running. Thank you Priya for the joy of seeing what you're working on and the greater joy of providing explanations that share both your excitement and understanding with me. Thank you Chris for making me feel like Caltech would be a good place to be during the visit and making that true during our time here. And for the best golf of my life. 감사합니다 형주 [8] for pushing me to excel academically in our first year, for earnest friendship, and for pouring hours into teaching me a little bit of Korean. Thank you Sriteja for joining me on the Dow project and helpful discussions. Thank you Chelsea for constantly reminding me that I have what it takes to succeed in academia and teaching me your secrets of success. The 202 has never been the same. Thank you Max for showing me what it means to believe in one's dreams and keep community, as well as for continuing to share your wisdom and kindness even after the 202. Thank you Sunday Nite Dinner for filling my first year and beyond with food and friendship. Thank you Nachi and Gunho for your steady friendship and making every dinner out with you a memorable one.

Widi, I thank the Lord that He placed you in my life through the random roommate process. When I languished, you listened; when I was cynical, you slipped in a sparkle of hope; when I floundered, you were firmly planted. You have helped me, comforted me, and shared a lifetime of the little joys and the big ones with me these past five years. Thanks for boba and pork belly, too. Thank you also for bringing Lena into our friend group, and Lena for always listening and bringing a special sense of quality to time spent together. Albert, thank you for entertaining my curiosities about language and science and for entertaining me with yours. Thank you for your persistent trek forward in life, your limitless fascination, your earnest encouragement of my doubted dreams, and your gentle willingness to teach, all of which have shown me what it means to be a good person. Thank you to the GCFunRunners for making Saturday mornings a weekly joy and for your patience as I learned to listen. Sami, thanks for sketching that picture of me; though just a

[8] "Thank you, Hyeongjoo." (Korean)

game, it somehow reminded me of a good piece of myself I had forgotten. Nathan, I would not have run the Rose Bowl half without your encouragement and belief in me. Your leadership of GCF really made my last year at Caltech a special one. Maria for sinners mass and meme mentorship. Hannah for asking all the right questions and listening for the answers. Thank you Rachel for patience and understanding. Thank you Tanner for showing me what it means to live out commitment to your faith, as well as for introducing me to BEMA. You've taught me a lot about myself and how to be a good friend. Mark for saying what needs to be said in the best way possible when everyone else is silent. Thank you to Grace for making micromeetups happen and, through them, community. Also for responding to my ribbing with tea and homecooked meals. Thank you to the SAFE team for showing me that faith can and ought to be part of my scientific self. Thanks to everyone in GCF for putting up with my antics and making Monday nights (and Tuesday tea, and Wednesday prayer lunch, and Friday movie nights, etc.) my favorite time(s) of the week.

Thank you to my students in Caltech's RISE tutoring program, Gael, Seldon, and Chris, who reminded me each week that knowledge's greatest power is the trust it forms when taught. A special thank you to my "two-dimensional person," Engels, whom I have tutored since he started high school: I'm proud to be your tutor. Շնորհակալութիւն[9] to the AGBU Choir for providing a community for me to be Armenian every week. The special joy of singing Komitas is not possible alone. Barb Catlin, Steve, Richard, Muir, Sophie, Iban, and Daniel, and the rest of the Caltech jazz band; Connor and David for jamming. Barb, thanks especially for believing in me after my hiatus from jazz in college and for teaching me how to be a confident and competent soloist on tenor. In the moments when I was least hopeful, I reminded myself that I would not be playing in a jazz band of this caliber had I not come to Caltech. There's nothing like playing with you all.

Der Sarkis, thank you for teaching me what it means to deeply care for a community by the care you've shown to the St. Gregory community, through happy times and sad. Deacon Aleksan for your persistent confidence in the good and bringing me along to volunteer at Union Station. Deacon Armand for being my first friend in Pasadena. You and your parents made me feel really at home here. Johnathan, John, Hagop, and all the rest for serving on the altar with me. Your growth encourages me. Deacons Hagop, Hagop, Manoug, Kevork, Hovsep, and Carl for your mentorship about church, life, and God. Garo for your inspiring

[9] "Gratitude" (Armenian)

dedication. Those at the Upland Church of Christ for reminding me of the beauties of a community small enough for everyone to be friends and look out for each other. David, thank you for getting me out of lab on Friday nights with your randomly timed and delightful phone calls. You never fail to remind me of the incomparable beauty of orthodoxy. Dn. George for opening my mind, heart, and soul to a new level of depth in the Bible and Armenian tradition. What I once ignorantly took for foolishness became a fountain of fascination in your lectures. Thank you to the whole St. Sahag community for your support for and interest in my PhD journey. You will always be my spiritual home and a joy to return to. Thank you especially, Der Tadeos, for making my time at St. Sahag so rejuvenating when I had the opportunity to visit home and for giving me a taste of home while I was away through your podcast, *Podmootiun*.

Thank you Anahid, Hasmik, Hagop, Natasha, and Lucine for your peace and prayer, which dispelled so many of my fears and doubts in my final year. Anahid, while the figures in this thesis—the good ones, at least—bear the mark of your eye for aesthetics, my gratitude for them is nothing compared to my gratitude for your friendship, even if by phone. Յակոբ, եղբայր ջան, thank you for giving me the best moments of the past five years. Thank you Natasha for commiserating about our PhDs over the years and for drawing me back to the things that matter most. My time in Boston with you two last summer left me forever changed. Թոմ ջան, ցավդ կանեմ, ախպեր[10]. Thank you for inspiring me with the beauty of poetry, language, and sincere friendship.

Շատ շնորհակալ եմ քեզի, Թանթ Սոսի, իմ հայերեն ուսուցչուհիս լինելու համար.[11]

Thank you Aunt Kris, Uncle Jerry, Keely (and Scott and Quinn), and Ben for always making times good when we got to see each other. Thank you Aunt Nora, Uncle Akram, Fares, Reena, and Cynthia for filling my time back home with family, even if it was usually cold.

Max, my brother, is the best. Whatever sense of humor and knack for good living I may have is thanks to you.

Thank you, Grandma, for always checking in and bringing simplicity to the complexities I saw in the decisions before me. Thank you, Grandpa, for still keeping an eye on me.

[10] "Dear Tommy, let me bear your sorrow, bro." (Armenian)

[11] "I am very grateful to you, Aunt Sossi, for being my Armenian teacher." (Armenian)

Thank you so much, Mom and Dad. I always knew I would do a PhD because I knew I wanted to be like you. You have given me more than I can ever return throughout each year I've spent on this earth. Dad, I would not know excellence if I had not learned it from you, nor would I have known how to approach writing a thesis. If this thesis in any way connects with its audience, it is because you showed me how to communicate why my work matters to others. Mom, thank you for calling and telling me it will be all right if I focus on having a good time in my PhD. I had sought to "fathom all mysteries and all knowledge" in my PhD, but you taught me that if I "do not have love, I am nothing." [12] Thank you for meeting my resistance with love.

Finally, to paraphrase St. Paul, I will "thank my God upon every remembrance of you, always, in every prayer of mine for you all, making request with joy." [13] Գոհանամ զքեն, Տեր Աստուած Մեր. [14]

[12] St. Paul's First Letter to the Corinthians, ch. 13, v. 2, New International Version
[13] St. Paul's Letter to the Philippians, ch. 1, v. 3–4, King James Version
[14] "I give thanks to you, Lord Our God." (Classical Armenian from Սբ.Պապպազ)

Abstract

Gas bubble nucleation is a fundamental phenomenon both throughout the natural sciences and in the production of foams for lightweight, functional materials; it is also the basis for many a bubbly beverage. Enhancing bubble nucleation in polyurethane insulating foams used for refrigeration can further reduce their low thermal conductivity without resorting to hazardous blowing agents used in the past. Experimental challenges of measuring the kinetics of the rapid, multiscale process of bubble nucleation pose a roadblock to investigation of suitable processing conditions, as well as the development of theoretical models of bubbles and foams.

Here, using a microfluidic flow-focusing technique developed for measurement of protein and chemical kinetics, we built a microfluidic cell to probe gas bubble nucleation of CO_2 in polyol, a model system for polyurethane insulating foams, at controlled pressure with millisecond resolution over acquisition times sufficient for optical, IR, and X-ray measurements. This technique allows for repeated measurements of bubble nucleation at any degree of supersaturation without the interference of heterogeneous nucleation from surfaces. By extrapolating a model fit to high-speed optical microscopy measurements of bubble growth backward in time, we estimated the degree of supersaturation at nucleation for thousands of bubbles. Estimates of the nucleation rate based on Poisson statistics were consistent with predictions by a string method model based on density functional theory and G-ADSA measurements. This model predicted that the addition of cyclopentane (a common physical blowing agent in polyurethane foams) can dramatically reduce the nucleation energy barrier due to the formation of a liquid-like layer of cyclopentane and CO_2 along the surface of the bubble that reduces the interfacial tension, which previous models have only predicted at significantly higher saturation pressures. This prediction was supported by thermodynamic measurement of a three-phase coexistence under similar conditions, which is a known fingerprint for such nucleation pathways, and measurement of significantly higher bubble nucleation rates upon the addition of cyclopentane. These findings shed light on the possibility of a previously unappreciated role of physical blowing agents like cyclopentane in enhancing bubble nucleation by opening up a qualitatively distinct and more favorable nucleation pathway.