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

Thesis by
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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.

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¹Book of Genesis, Chapter 1, verse 31, King James Version
²St. Paul’s Letter to the Romans, ch. 5, v. 3–4, New International Version
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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)
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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)
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7 Thank you Sammy for your friendship. I learned a lot of Arabic from you.” (Arabic)
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\footnote{8\text{“Thank you, Hyeongjoo.” (Korean)}}
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9 “Gratitude” (Armenian)
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Dear Tommy, let me bear your sorrow, bro.” (Armenian)

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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)
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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 Յուրաքանչյուր)
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.