IMPLOSION OF ULTRASOUND-GENERATED NANOBUBBLES TO DESTROY PFAS IN CONTAMINATED WATER

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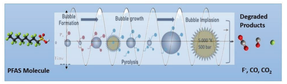
INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are persistent contaminants that are resistant to conventional treatment and require effective destruction technologies. This project investigates PFAS mineralization via the implosion of ultrasound-generated nanobubbles, which creates extreme localized temperatures and pressures as well as highly reactive radical species (e.g., •OH, •H) capable of cleaving strong C-F bonds through coupled pyrolytic and radical-mediated pathways.

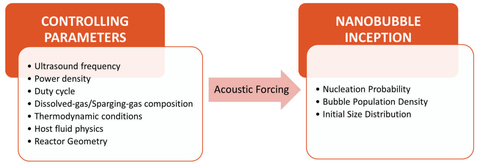
The research integrates three main interconnected tasks. **Task 1** develops a nucleation framework linking nanobubble formation to ultrasound frequency, acoustic intensity, dissolved-gas/sparging-gas composition, and impurities such as PFAS. **Task 2** models bubble oscillation and collapse using Rayleigh-Plesset-based formulations, incorporating PFAS-modified interfacial effects. **Task 3** employs reactive molecular dynamics (MD) simulations to resolve PFAS adsorption and bond-breaking behavior at nanobubble interfaces, supported by ongoing liquid chromatography–mass spectrometry (LC-MS), inductively coupled plasma–mass spectrometry (ICP-MS), and fluoride ion analysis. LC-MS quantifies residual PFAS and intermediates, while ICP-MS measures released fluorine to confirm mineralization efficiency.

Together, these efforts establish a multiscale framework that links cavitation physics to PFAS mineralization, directly informing the optimization of a field-scale nanobubble reactor **(Task 4)** for improved energy efficiency and scalable treatment performance.

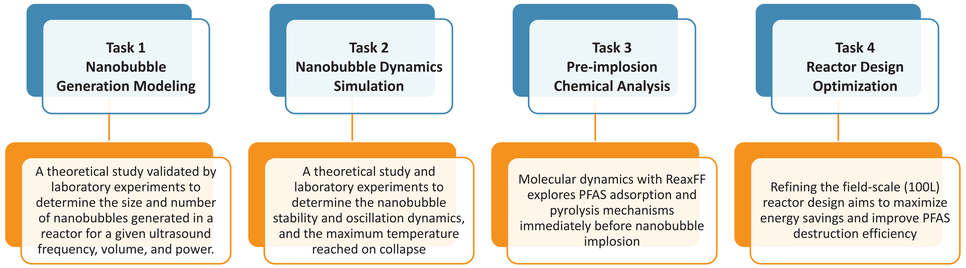


LITERATURE REVIEW [TASK 1]

- **Nanobubble nucleation governs performance**. Nanobubble generation is the primary control layer in ultrasound-driven systems
- **Heterogeneous nucleation dominates** in practical reactors, where pre-existing nuclei-such as dissolved gas/air pockets, surface crevices, suspended impurities, and solid interfaces-lower the energy barrier for bubble nucleation; homogeneous nucleation defines only a thermodynamic limit
- Nanobubble formation is **probabilistic but tunable** through ultrasound frequency, power density, duty cycle, dissolved gases/sparging gas, and reactor geometry



OBJECTIVES/ TASKS



- Multiscale modeling (molecular → continuum) reveals deviations from classical nucleation theory under dynamic acoustic forcing
- Experimental diagnostics link nucleation physics directly to peak collapse conditions and radical production
- **Nanobubble population statistics ultimately dictate contaminant degradation efficiency**

NANOBUBBLE DYNAMICS [TASK 2]

How nanobubbles evolve from formation to implosion

- After nucleation, nanobubbles are subjected to time-varying acoustic pressure, leading to cyclic growth/ collapse oscillations
- Bubble behavior is modeled using **Rayleigh–Plesset**–based formulations, which predict time-dependent bubble radius R(t) under acoustic forcing,

$$R\frac{d^2R}{dt^2}+\frac{3}{2}\left(\frac{dR}{dt}\right)^2=\frac{1}{\rho_l}\left[P_g(t)-P_a(t)\right]-\frac{4\nu_l}{R}\frac{dR}{dt}$$

where physical variables are P_a is the applied acoustic pressure, Pg is the pressure in the bubble, and liquid properties (viscosity - v_l and density - ρ_l).

- During rarefaction, bubbles expand slowly; during compression, they undergo **rapid, near-adiabatic collapse** (see Fig. 1), generating:
  - Temperatures ~5,000 K
  - Pressures ~500–1,000 atm
  - Shock waves and radical (e.g., •OH, •H) formation
- Peak collapse conditions depend on:
  - Acoustic pressure amplitude
  - Ultrasound frequency (750–1000 kHz)
  - Liquid properties (viscosity, density)
  - Gas content and interfacial conditions
- Model predictions of nanobubble dynamics are validated using complementary diagnostics. Calorimetry measures acoustic power dissipation, KI dosimetry quantifies hydroxyl radical production, and sonoluminescence techniques detect high-temperature collapse events.

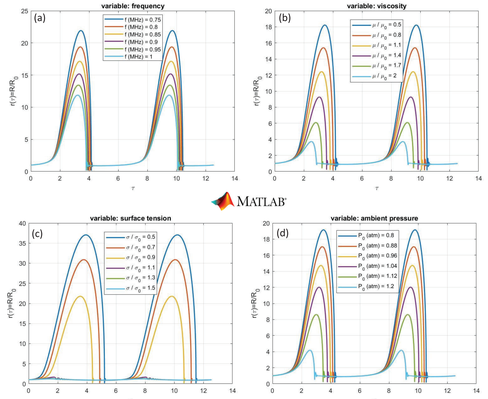
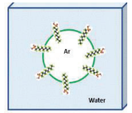


Figure 1: The influence of four relevant parameters on the bubble dynamics: (a) acoustic frequency f, (b) liquid viscosity (relative to that of pure water), (c) bubble surface tension (relative to that for a pure argon/pure water interface), and (d) ambient pressure P_0.

Figure 1 shows the normalized bubble radius r(τ) as a function of nondimensional time **τ**, which is in units of 2π/f. All simulations assume an initial bubble size, R_0 = 150nm, and that the physical parameters are at their standard values (ambient pressure, P_0 = 1 atm, viscosity of water, μ_0, surface tension for air/water, σ_0, and acoustic frequency, f = 0.95 MHz. Clearly, each parameter has a strong influence on bubble dynamics, and we plan to analyze this influence in more detail to provide results that will also be useful for further experimental research.

JUST BEFORE NANOBUBBLE IMPLOSION [TASK 3]

- This task investigates the molecular-scale interactions between PFAS molecules and nanobubbles immediately prior to implosion during acoustic cavitation, integrating MD simulations with experimental characterization.
- At collapse, the nanobubble behaves as a microreactor, with pyrolysis occurring in the bubble core and at the gas–liquid interface
- Amphiphilic PFAS (e.g., PFOS, PFOA) preferentially adsorb at the gas–liquid boundary due to hydrophobic tail interactions, while electrostatic effects influence adsorption strength.
- To study this, we model argon nanobubbles (NBs) in an aqueous environment using LAMMPS and simulate under both NVT and NPT ensembles for 20 ns to evaluate NB stability, interfacial structure, and thermodynamic behavior in water.



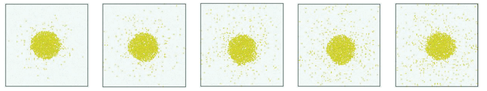


Figure 2: Snapshots of Argon nanobubbles (50 Å) in a water box (size 237.8 Å) under NVT conditions for 10ns

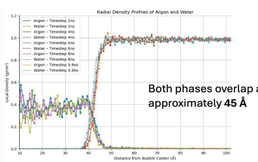


Figure 3: Gas and Liquid density profile with respect to distance from the bubble radius under NVT conditions

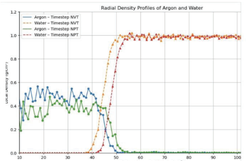


Figure 4: Gas and Liquid density profile with respect to distance from the bubble radius under NVT & NPT conditions

- Figures 2–4 illustrate MD simulations of argon nanobubbles in SPC/E water under NVT and NPT conditions. Time-resolved snapshots (Fig. 2) confirm the stability of a 50 Å nanobubble over 10 ns. Radial density profiles (Fig. 3-4) quantify phase separation and define the gas–liquid interface, demonstrating a well-resolved interfacial boundary.
- These results establish the baseline nanobubble geometry and stability necessary for subsequent PFAS adsorption and pre-implosion chemical analysis.
- PFAS degradation is evaluated using complementary analytical techniques. LC-MS quantifies residual PFAS and transformation products, while ICP-MS and fluoride analysis measure released fluorine to confirm defluorination and mineralization. Together, these methods verify both the removal of the compound and the recovery of elemental fluorine.

CONCLUSION

- Nanobubble nucleation, dynamics, and interfacial chemistry jointly govern PFAS destruction efficiency
- Heterogenous nucleation controls nanobubble population statistics, which determine collapse behavior under acoustic forcing
- Nanobubble oscillation and near-adiabatic implosion generate extreme thermodynamic conditions and reactive radicals that drive C-F bond cleavage
- PFAS adsorption at nanobubble interfaces directly couples cavitation physics to molecular-level degradation mechanisms
- Multiscale integration (nucleation modeling, Rayleigh-Plesset dynamics, and reactive MD simulations) provides a predictive framework linking acoustic parameters to mineralization outcomes
- These mechanistic insights directly inform refinement of a field-scale reactor to improve energy efficiency and scalable PFAS treatment performance

FUTURE WORK

Task 1 – Nanobubble Generation

- Integrate Task 1 nucleation predictions with Task 2 dynamics results to identify overlapping operating regimes that maximize bubble generation and ensure stable oscillation.
- Refine acoustic threshold and growth models using insights from Holland–Apfel theory. Determine parameter windows that optimize nanobubble density while maintaining collapse conditions suitable for high-temperature PFAS degradation.

Task 2 – Nanobubble Dynamics

- Complete stability analysis of single-bubble oscillations, including two types of instability: Rayleigh–Taylor instability and parametric instability.
- Identify parameter ranges (R_0, acoustic pressure, frequency) that produce >5000 K peak temperatures while maintaining spherical stability.

Task 3 – Just Before Nanobubble Implosion

- PFBA molecules are introduced (**Fig. 5**) into the previously validated MD nanobubble system to quantify interfacial adsorption, bubble-size effects, and head–tail orientation at the gas–liquid boundary.
- Continue complementary laboratory experiments to provide new data on nanobubble size, concentration, and Zeta potential under pressure variations

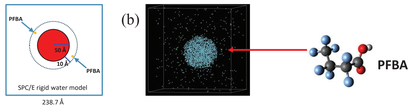


Figure 5: (a) Schematic representation of the PFBA molecule placement in the water box within the area 10 Å away from the NB surface, and (b) initial simulation model of Ar NB in a water box with PFBA molecules within the 10 Å away from the NB surface using LAMMPS.

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