# Even more accelerated acoustic prediction of aging and failure

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## 1. Overview

Industrial dispersions are designed using colloidal systems with various types of interactions. The interactions generate non-equilibrium properties that lead to long product shelf lives, but it is also precisely these properties that lead to the products' eventual destabilization and failure. Thus, there is great interest in developing accelerated aging protocols to screen for stable formulations, but classical aging methods such as heating and centrifugation do not capture the full cascade of mechanisms responsible for the natural aging of commercial formulations. One reason is that many materials are temperature-sensitive and undergo irreversible changes when heated. Another reason is that centrifugation only enhances the effect of gravitational loading on a non-density matched dispersion at that current time point, but does not increase the speed of thermally driven mechanisms such as Ostwald ripening or flocculation.

In other words, heating or centrifuging often distort real stability mechanisms, leading to incorrect shelf-life predictions and unreliable correlations between accelerated and natural aging pathways. **Acoustic aging promises to preserve chemistry and interfacial structures, accelerating only mechanically activated processes, therefore shortening formulation development.** The need for an alternative, reliable, and mechanism-faithful aging protocol is widely recognized across IFPRI member companies, as reflected in feedback and discussions from the AGM and liaison meetings.

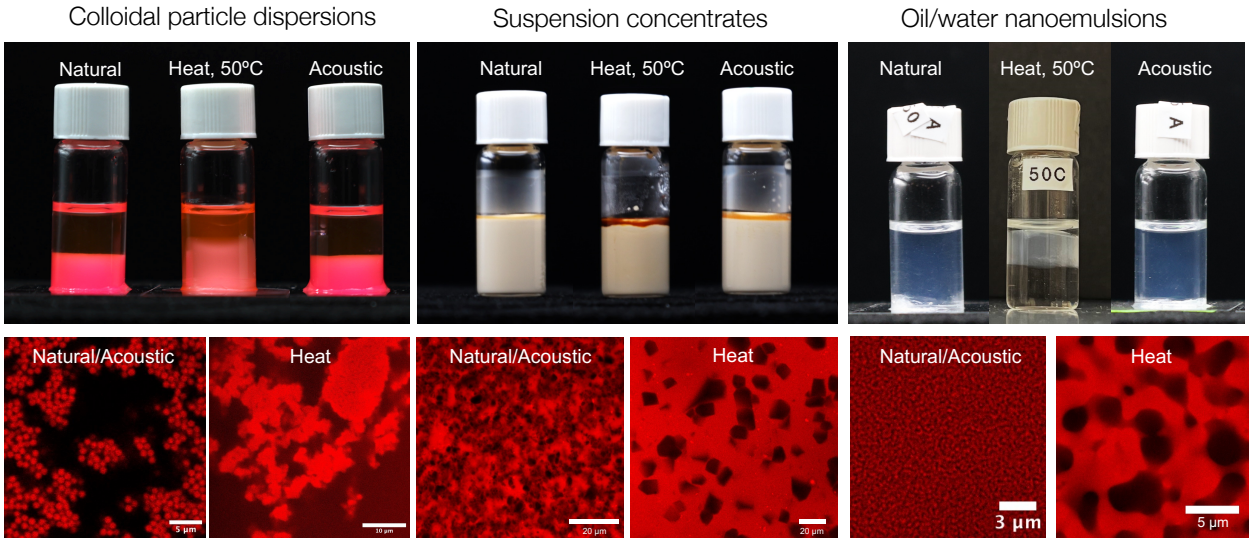



**Figure 1.** Results from Phase I of IFPRI project on accelerated aging using acoustic waves show that it is possible to accelerate aging while maintain the fidelity of natural aging mechanisms of a broad class of formulations including particle dispersions, suspension concentrates (from IFPRI member), and oil/water nanoemulsions. Here the (top) photographs are pictures of multiphase wet systems aged in different ways, demonstrating macroscopic phase separation, along with (bottom) their respective microscopy images showing destructive effects of mild heat aging.

*Current status:* This renewal project will build upon the promising proof-of-concept results in which we demonstrate that **low-power ultrasound does indeed speed up the natural aging of a broad dispersion class. Figure 1** shows that ultrasound accelerates without destroying samples, unlike heat aging. Thus far, we have achieved acceleration factors of 1.5-5x in emulsions, gels,

and capsule suspensions, and academic manuscripts are in preparation by two doctoral students supported on this project.

The first three years of the IFPRI project were focused on the design of a working acoustic setup compatible with confocal microscopy, demonstrating that low-power acoustic waves are capable of accelerating the destabilization kinetics of multiple dispersion classes, and determining the effect of acoustic and material parameters on the acceleration factor. The results have gathered significant interest from IFPRI members during AGMs and during regular liaison meetings with member companies including Dow, Nestle, FMC, and Cargill. Some outstanding questions have arisen from these discussions:

1. Can acceleration factors be further improved through process optimization?

   *Industry requires speed without sacrificing fidelity. If acoustics can produce larger acceleration factors while reproducing the same modes of failure, then companies can replace months of stability tests with minutes of acoustics exposure.*

2. How exactly does ultrasound speed up aging for different classes of dispersions?

   *We do not want any accelerated aging approaches to introduce artifacts (chemistry, cavitation, or other unnatural degradation). A mechanistic foundation will convert the method into a reliable predictive tool.*

3. Why is there a universal delay prior to phase separation?

   *This induction time could perhaps serve as an early warning sign of instability, and has been reported extensively in colloidal and granular systems. Formulations could be designed to extend this delay period which encodes information about microstructural precursors to failure.*

4. Is the acoustic aging method scalable to larger volumes?

   *Industrial QC/R&D pipelines require analytical methods that can handle large samples or even in-line monitoring. If the acoustic aging scales in a predictable manner with sample size and acoustic parameters, then it has potential to be incorporated into standardized quality control.*

In Phase II of this project, we plan to address these questions and to continue improving the acoustic testing protocol on IFPRI-relevant systems. Of key interest is the mechanism through which acoustic waves accelerate the natural aging process. Do components scatter acoustic energy which then somehow translates to an increased effective diffusion coefficient? Does the phenomenon arise from streaming effects of the solvent around boundaries? The mechanistic insights are important and are uniquely addressed by IFPRI academic partnerships because they allow us to extend and translate the method to an even broader class of materials, to push the limits of the acceleration factors that can be achieved using acoustic aging methods, and to determine if the process is ultimately scalable or not.

**Impact:** If successful, this IFPRI project will generate a new, non-destructive analytical method through which a broad class of wet dispersions could be aged accurately.

**Proposed timeline:**

<u>Year 4: Investigate mechanisms of micro/macro-phase separation</u>

- Modify acoustic transducer, positioning, and process protocol
- Track acceleration factors as a function of acoustic energy and material properties
- Obtain particle/droplet size distribution and other microscopic parameters
- Track particle dynamics and velocity when acoustic waves are applied

<u>Year 5: Increase acoustic acceleration factor</u>

- Determine if acceleration factors follow Arrhenius scaling
- Determine shift factors for microscale destabilization and macroscale phase separation
- Target microscopic precursors to macroscale phase separation

Year 6: Validate acceleration factor across multiple formulation types

- Measure acceleration factors for a broad variety of samples including emulsions, dispersions, viscosity-modified formulations, and encapsulated suspensions
- Perform feasibility estimates for process scale up

*Hypothesis*: Acoustic waves accelerate aging by increasing the frequency of barrier-crossing events in the early stages of destabilization without changing the thermodynamic pathways (**Figure 2**).

## 2. Phase I Findings and Significance

Particle-level interactions are engineered into wet dispersions to provide a variety of functionalities including but not limited to viscosity modification, thermal and electrical conductivity, and active ingredient encapsulation. These nanoscale interactions lead to non-equilibrium behavior that eventually destabilize the dispersions, starting with microscopic phenomena such as coalescence and flocculation, and eventually developing into macroscale sedimentation or creaming.[1] Below is a summary of the major findings from the project in Phase I.

*Macroscopic phase separation occurs more rapidly*—Acoustic waves are mechanical perturbations that speed up various microscale destabilization processes.[2-4] In our nanoemulsion samples where oil droplets are suspended within a surfactant-laden solution,[5] the macroscale phase separation consistently occurs more rapidly when acoustic waves are applied (**Figure 2a**). The opaque layer at the top forms due to droplet size growth (**Figure 2b**) and creaming from the lower density of the oil droplets with respect to water. Note that the time on the *x*-axis refers to waiting time and not the acoustic exposure time, which is kept constant at 1 hour. The results suggest a possible temporal shift factor that can rescale the particle diameter. If this scaling works, then it indicates that we have successfully accelerated the natural aging process with full fidelity at the droplet level. We are also more rigorously fitting the particle size distribution (not shown here) to the Liftshitz-Slyozov-Wagner theory[6,7] and population balance models[8] to determine if acoustics are enhancing Ostwald ripening or coalescence. Results suggest it is the latter.

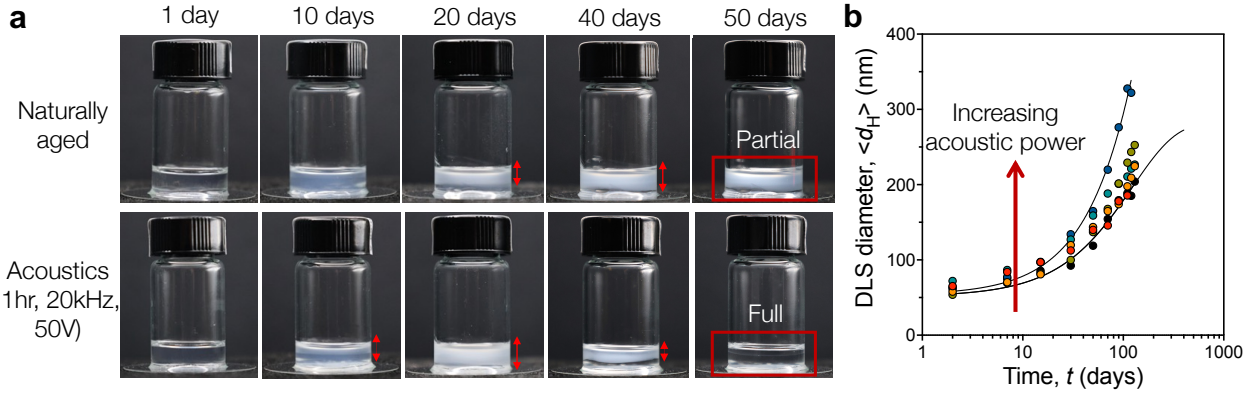



**Figure 2.** (a) Demonstration of acoustically accelerated phase separation in nanoemulsions. The samples that have been exposed to low-power acoustic waves for 1 hour showed faster and more complete macroscale phase separation. (b) Dynamic light scattering results show that the droplet sizes increase with increasing applied acoustic power.

*Acceleration of delayed creep in colloidal systems*—A similar shift in the macroscopic phase separation behavior is seen with weakly flocculated systems including an IFPRI sample of suspension concentrates and in a colloidal gel as shown in **Figure 3**. The suspension concentrates are agrochemical formulations provided by an IFPRI member. Although heat aging at 50ºC generated a higher acceleration factor than acoustics, microscopy analysis shows that

irreversible melting of active ingredients took place. Here we defined the acceleration factor as the ratio of the natural phase separation time and the acoustically induced phase separation time. A similar behavior is observed with a colloidal depletion gel made out of poly(methyl methacrylate) colloids suspended in an organic solvent. The systems show delayed creep, which is well studied in colloidal gel literature and has been attributed to a stress-bearing length scale and the growth of streamers. Heating the colloidal gel caused irreversible clumping, while acoustic perturbation led to a ~1.5x decrease in the sedimentation timescale.

## 3. Technical Background

Aging in industrial dispersions is controlled by thermally activated rearrangements at the particle or droplet scale, where the relevant barriers are on the order of a few $k_BT$. A number of different mechanisms may lead to macroscopic phase separation and these mechanisms are often specific to each type of dispersion.[1]

In nanoemulsions with very low oil solubilities (<$10^{-6}$ g/g), destabilization proceeds almost entirely through coalescence rather than Ostwald ripening. The coalescence rate is governed by the Smoluchowski collision rate and by the hydrodynamic film-drainage time, which depends on interfacial viscosity, surfactant bending modulus, and Laplace pressure.[7,9] Deviations from the canonical Ostwald ripening law therefore indicate a shift into film-rupture-limited growth. In Phase I, a 1-hour low-power acoustic exposure measurably shifted the entire droplet size distribution which is consistent with enhanced coalescence rather than surfactant desorption or thermodynamic alteration. Acoustic waves are likely acting directly on the transport and drainage processes that govern droplet-droplet dynamics without modifying the surfactant adsorption.

In suspension concentrates (SCs), destabilization kinetics arise from the interplay between gravitational forcing and weak interparticle attractions.[10] Heating SCs can alter their viscosity, shifts the surfactant behavior, and in some cases melts the active ingredient. Because acoustic pressure amplitudes in the $10^2$-$10^3$ Pa range (below cavitation thresholds) introduce streaming effects that enhance local rearrangements[3] but preserves the chemical environment, acoustic-aged SCs from IFPRI members reproduced the natural sedimentation pathway while heat-aged samples did not.

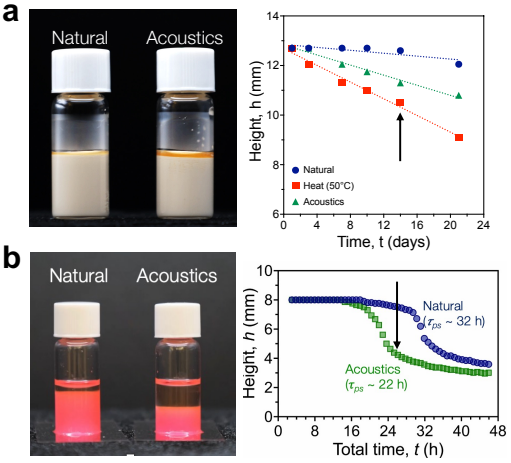



**Figure 3.** Acoustics accelerates the phase separation of (a) suspension concentrates from IFPRI member, and (b) a weakly flocculated colloidal depletion gel. We track sediment heights as a function of time to obtain acceleration factors.

In depletion gels formed by colloids interacting with nonadsorbing polymers, the dominant microstructural processes include bond rupture, cage escape, and large-scale network collapse.[11-13] The networks in weak gels (1-10 $k_BT$) respond elastically at short times but undergoes delayed collapse at long times through streamer formation.[14] This behavior is consistent with the delayed-creep framework reported in the literature, where gels subjected to a constant sub-yield stress exhibit an extended primary creep regime followed by sudden accelerations in strain rate once localized bond-breaking events percolate through the network.[15-17] The creep rate obeys a power-law form until a critical microstructural transition triggers rapid deformation and collapse.[18] The collapse time distribution in such systems is well described by Weibull-type statistics due to cooperative, nonlocal rearrangements. Acoustics feed directly into

this failure pathway by increasing the frequency of local bond-rupture attempts and accelerating the transition from primary to tertiary creep without altering the depletion potential.

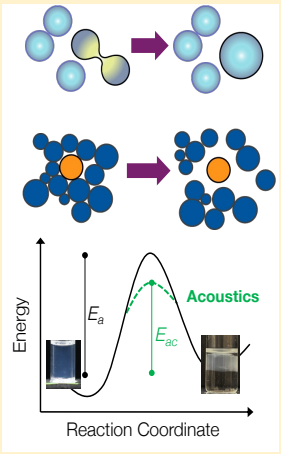
Across the dispersion classes described above, the common control variable is the rate of rare, barrier-crossing events: film rupture between droplets, bond rupture in weak gels, or the emergence of high-mobility "hot spots"[19] whose strain rates exceed the background by orders of magnitude. These events control the induction period and determine the macroscopic aging time. A field that increases the frequency of these events by even a modest factor is likely to produce nonlinear reductions in the observable lifetime. Low-power acoustics increase the local dissipation rates and generate nonaffine displacements that preserve the thermodynamic landscape. Phase I established this at proof-of-concept level, but the quantitative rate laws, scaling relationships between acoustic energy and destabilization kinetics, frequency-dependent mechanisms, and generality across formulation classes remain unresolved. These technical gaps motivate the proposed renewal and define the central scientific questions for Phase II.

Implications for industrial formulations:

Emulsions—Acoustics are likely to increase droplet-collision and film-drainage coalescence processes.

Flocculated dispersions—Acoustics should increase the frequency of the small bond-rupture and rearrangement events that control delayed collapse in weak networks and speed up the same phase separation mechanisms that occur during real storage.

**Acoustics should increase the rate of the barrier-crossing steps that trigger macroscopic failure**, producing faster yet mechanism-faithful aging for wet dispersions.




## 4. Research Plan

### Aim 1: Identify microscopic mechanisms of acoustically enhanced destabilization

This aim will focus on directly observing how acoustic fields perturb microscale structure in emulsions, gels, and suspension concentrates. We will perform controlled acoustic exposures while tracking particle or droplet size evolution using dynamic light scattering (DLS) and confocal microscopy. Specific experiments will include measuring size distributions before and after fixed acoustic treatments of varying durations (between 5 minutes to 24 hours) and quantifying rate laws that govern growth or structural rearrangement. These data will allow us to determine whether coalescence, flocculation, or another mechanism dominates under acoustic stimulation.

We will also track particle dynamics and droplet motion during acoustic excitation. Using tracer-based imaging and velocimetry, we will measure local displacement fields and use metrics including mean squared displacements and self-correlations to determine whether aging acceleration arises from increased effective diffusivity, boundary-driven streaming, or small-amplitude interfacial oscillations. These measurements will be conducted as a function of acoustic power and frequency to identify thresholds for activating different modes of microscopic motion.

We will also measure early-stage structural signatures that precede phase separation which includes quantifying induction periods by monitoring initial growth of creaming layers or sediment height changes at high temporal resolution. For gels, we will characterize changes in creep compliance during short acoustic pulses to see whether microstructural softening correlates with later collapse. These measurements will map specific microscopic events to the macroscopic acceleration observed under acoustic stimulation.

**Aim 2: Define and increase acceleration factors**

This aim will quantify how rapidly acoustics can accelerate destabilization and determine how acceleration scales with controllable parameters. For each formulation type, we will vary the acoustic power, frequency, cycling and exposure time, then measure how the dispersions behave through parameters including the sedimentation rate, droplet growth rate, and creep-to-failure timescales. The resulting datasets will allow us to construct acceleration functions, defined as $\tau_{nat}/\tau_{acoustic}$ for either macroscopic or microscopic parameters, across a broad parameter space.

We will also examine whether acceleration factors obey predictive scaling laws. One approach is to test Arrhenius-like relationships by plotting acceleration factors against input acoustic energy density. If the data fall on a universal curve, then it may be evidence that the acoustic shift is representative of true natural aging mechanisms. Another approach is to determine whether shift factors can be applied to collapse curves of droplet growth or sediment height across different acoustic conditions. If shift factors exist, they would directly translate acoustic-aging results into natural-aging predictions.

To extend acceleration factors beyond the 1.5-5× range achieved so far, we will tune the experimental conditions that most influence energy delivery. This includes adjusting transducer position, the acoustic coupling medium, and vial geometry to reduce attenuation. We will also test continuous versus pulsed acoustic exposure to determine which waveform most efficiently accelerates destabilization without introducing artifacts. These optimizations are essential to defining the upper limits of acceleration achievable with this method.

**Aim 3: Demonstrate generality and scalability**

Aim 3 evaluates whether acoustic aging is sufficiently general and scalable to serve as a standardized accelerated testing protocol for IFPRI members. Phase I demonstrated accelerated aging in nanoemulsions, colloidal gels, and an agrochemical suspension concentrate, but industrial applications require a broader set for validation. We will extend testing to include viscosity-modified formulations, encapsulated suspensions, concentrated dispersions, and other complex fluids, explicitly aligning with the proposal's Year 6 plan to measure acceleration factors across diverse sample types. This will allow us to determine whether different material classes exhibit consistent acceleration behavior or whether formulation-specific calibrations are required.

Generality also depends on reproducibility across systems. We will therefore perform comparative analyses of sedimentation kinetics, droplet-coalescence dynamics, delayed creep behavior, and induction periods across multiple materials. These parallel datasets will reveal how acoustic aging speed correlates with flocculation strength, viscoelasticity, and particle packing. Furthermore, to evaluate scalability, we will perform scale-up assessments and focus on how sample volume, container geometry, and acoustic attenuation influence acceleration factors. This includes testing whether the method remains predictive when applied to larger volumes or when integrated into continuous or in-line systems. By establishing generality across formulations and verifying scale-up potential, Aim 3 will determine whether acoustic aging can evolve from a laboratory demonstration into a practical, broadly deployable method for stability prediction in industrial R&D and quality control pipelines.

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