

A Soft 3D Acoustic Metafluid with Dual-Band Negative Refractive Index

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Advanced devices for imaging, sensing, cloaking, etc., with an unprecedented control of the propagation of waves are expected to emerge from the advent of metamaterials.^[1] For these rationally designed composites, engineering the material properties already led to exciting demonstrations, mostly but not only in the realm of electromagnetism.^[2–4] For proof-of-principle purposes, fabrication techniques are being progressively scaled down from hand-made materials to top-down technologies such as nanophotolithography,^[5] or even sub-micron 3D printing,^[6] and indeed extraordinary metaproperties are currently blossoming in several fields.^[4] Yet, the need of a raw metamaterial, functional and processable, available in large quantity and fairly easy to fabricate, will soon emerge for practical implementation into devices.

Here, we focus on ultrasonic fluid materials and specifically on the subclass of bulk, 3D homogeneous metafluids embedding locally resonant inclusions (LRIs) that are much smaller than the incident wavelength of the ultrasonic wave. The LRIs need not (but may) be ordered, and the properties of the final homogeneous material mainly emerge from the resonances that the inclusions display.

We also follow the soft matter route, which combines a bottom-up strategy with physical chemistry and microfluidics.^[7] We recently demonstrated that such an approach is versatile enough to yield amorphous 3D metafluids for acoustics^[8] and 3D metamaterials for optics.^[9]

From a chemical engineering prospect, most processes for making these materials are upscalable and physical chemistry offers a fantastic panel of routes for their conception—from plastics to ceramics—which often delivers soft, fluid-like materials; fluid processes are thus accessible with here again

a large choice: moulding, coating, 3D-printing, etc. Ultimately, advanced plastics, paints, coatings, films, devices, etc., integrating the acoustic raw metamaterial is becoming realistic.

At the heart of such a material lies the LRI. Our recent demonstration of a 3D soft acoustic metafluid was based on a simple approach:^[8] negative index in ultrasounds is achieved by adding large quantities of fairly calibrated “ultra slow” inclusions in a fluid matrix. “Ultra slow” refers to the very low sound speed in the LRIs ($\approx 100 \text{ m s}^{-1}$, typical of porous materials) as compared to the one in the aqueous matrix ($\approx 1500 \text{ m s}^{-1}$), and which can excite Mie resonances. Such an “acoustic cream” may display a negative index over a significant frequency range where monopolar and dipolar Mie resonances overlap.^[10]

Here, using theory and experiments, we investigate more in details the impact of the mechanical properties of LRIs on the effective response of the acoustic cream and specifically the possible mode conversion at the level of spherical LRIs. Indeed, while only longitudinal waves within the scatterers are usually considered, shear waves being neglected,^[1,8,11] the latter may also induce additional Mie resonances^[10,12] and impact the overall acoustic response of the material.

We chose silica nanogels as candidates for LRIs because they not only exhibit a modest sound speed ($\approx 50–300 \text{ m s}^{-1}$ depending on their density) but they are also fairly rigid (Poisson's ratio $\nu \approx 0.2$, also density-dependent) and are thus likely to sustain significant shear waves. Digital microfluidics permitted us to synthesized highly calibrated spherical xerogel beads thanks to the exquisite liquid templates the tool delivers, into which a gelation kinetics of silica was achieved. These gelled drops were then dried, surface functionalized, dispersed into a fluid matrix and characterized as acoustic dopants (for the most relevant ones in terms of mechanical properties screened at the level of individual LRIs).

Unlike most microfluidics studies, we chose the alkaline route for matching acoustic literature, and also because the one-pot process we describe below is particularly simple and well suited to microfluidic implementation.^[14–16] The reaction (i.e., formation and gelation of a silica sol) is achieved by mixing equal volumes of two reactive solutions, one containing the silica precursor in ethanol and the other one the catalyst in water, and leads to an aggregated state of nanoparticles. We adapted the stoichiometry (see the Supporting Information) to induce macroscopic gelation within $\approx 10 \text{ min}$, as assessed by visual inspection of the tilted macroscopic sample. A detailed kinetic study in bulk (Figure S1, Supporting Information) evidences that hydrolysis and condensation of the silica precursor are concomitant, and are completed in a few minutes, whereas

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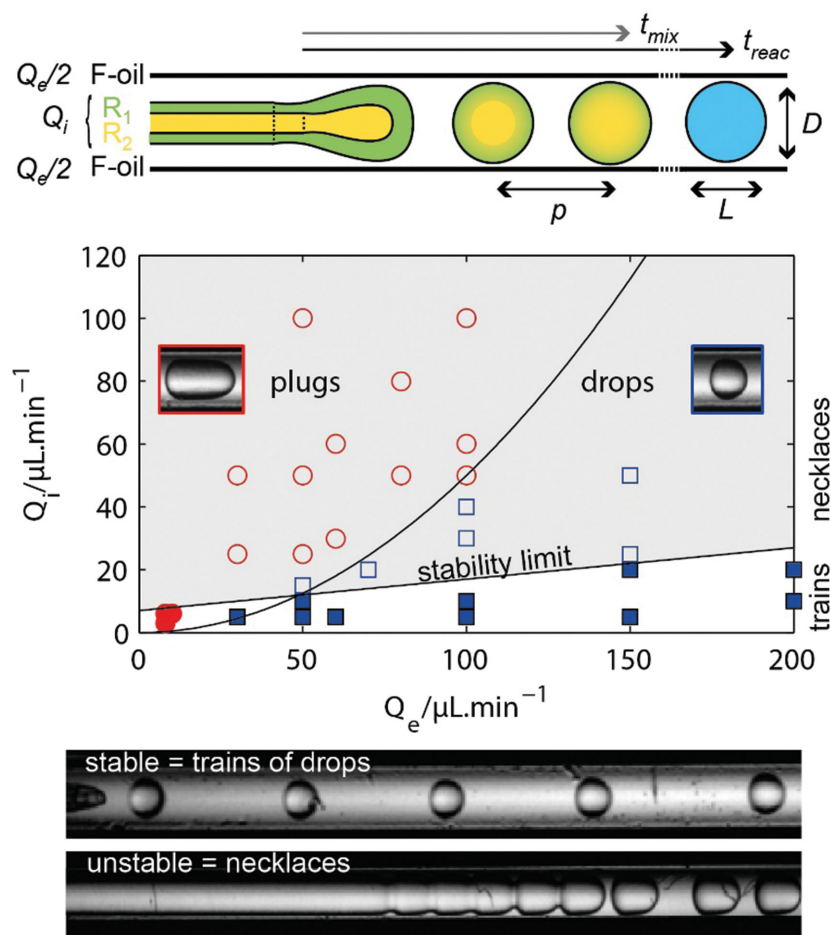


Figure 1. Top: schematic microfluidic setup where two nested fused-silica capillaries (outer-coating of polyimide, inner home-made coating of Dyneon, respective inner and outer diameters: 74 and 152 μm and 179.5 and 354 μm) deliver each a reactant (R_1 and R_2 for the silica precursor and the catalyst) required for the sol-gel process; the reactants meet and form droplets in a continuous stream of fluorinated oil (F-oil, FC40) within a perfluoroalkoxy alkane (PFA) tubing (762 μm inner diameter). Important for the chemical process are: i) the mixing time t_{mix} , ii) the reaction time t_{reac} , the distance p between drops and their aspect ratio L/D . Middle: the flow diagram shows that a segmented flow (drops or plugs) is created in all conditions, with squared solid symbols for spherical drops only ($L/D = 1$). Bottom: the train of drops may become unstable, which induces coalescence or necklace formation, and the stability zone is shown with solid symbols on the flow diagram.

gelation is a slightly longer process and takes actually ≈ 6 min in our conditions.

On chip, the reaction is achieved by contacting equal volumes of the two reactants in a three-level nested-capillaries microsystem (Figure 1, top) producing ≈ 500 μm diameter droplets carried by an inviscid fluorinated oil (F-oil, Figure 1, top). Mixing is fairly fast ($t_{\text{mix}} \leq 20$ s, Figure S2 in the Supporting Information) due to the concentric injection configuration, and actually fast enough as compared to the chemical kinetics to ensure appropriate chemical conditions ($t_{\text{mix}} \ll t_{\text{reac}}$, the reaction time).

We focus on the specific region of the flow diagram (Figure 1, middle) illustrated with squared symbols where the drops are spherical. Importantly, we observe that the trains of drops may become unstable, with a fluctuating period p between drops

that leads to aggregation and partial coalescence of the particles. This necklace regime (shaded region of Figure 1, middle) is undesirable and prevents the production of individual objects: the working conditions are thus limited, as highlighted by solid symbols on the flow diagram. These conditions yield a stable rate of particle production ($\approx \text{Hz}$, i.e., 10^5 particles per day).

The length of the reactor (> 2 m) is chosen so that the residency time of the drops is of the order of 10 min, thus ensuring *in situ* gelation, and we indeed collect gelled wet particles at the outlet of the device, see Figure 2a, the size distribution of which is fairly peaked ($R_{\text{wet}} = 280 \pm 8$ μm , inset of Figure 2a from which we define the size dispersity as $cv = \sigma / R$ where σ stands for the standard deviation around the mean radius R).

Postprocessing of the particles is of prime importance. First, the particles are matured into F-oil for 24–48 h, which tends to consolidate the gel. Then, the particles are phase transferred into ethanol to stop the condensation reaction and washed repeatedly with ethanol to remove water. The first washing bath may contain 10 vol% hexamethyldilazane (HMDS) which will both add up hydrophobicity to the final gel and will prevent a too strong consolidation of the gel upon final drying. This ultimate drying stage is achieved in air on an absorbing tissue and leads to spherical xerogels (Figure 2b,c,d1,d2) with a peaked size distribution and a low polydispersity ($R = 180 \pm 6$ μm , inset of Figure 2a, $cv \approx 3\%$). Finally, to make the particles dispersible in a water-based matrix, we used plasma oxidation to turn the outer surface of the particles hydrophilic while preserving the inner hydrophobicity. Figure 2f shows a successful dispersion of xerogel beads into carbopol (a yield-stress aqueous gel), whereas Figure 2g illustrates the failure to disperse the particles when the

outer surface is not rendered hydrophilic.

A key point for generating an efficient LRI is that it should display a very low sound speed, which porous materials are known to achieve. As the sound celerity scales as $c \approx \sqrt{K/\rho}$ with K as an elastic modulus and ρ the density, the right combination of these two quantities—which is largely tunable via the sol-gel chemistry and postprocessing—may indeed select a low sound speed. We thus measured their density and Young's modulus at vanishing frequency as a guide to select the most efficient LRIs. First, the particles we synthesized are indeed porous, as confirmed by nitrogen adsorption isotherms (Brunauer-Emmett-Teller analysis of the specific surface 550 ± 50 $\text{m}^2 \text{g}^{-1}$, pore size 10 ± 1 nm, not shown) and also using electron microscopy at several scales (SEM, Figure 2e, and HR-TEM after microtome, inset of Figure 2e). Their density

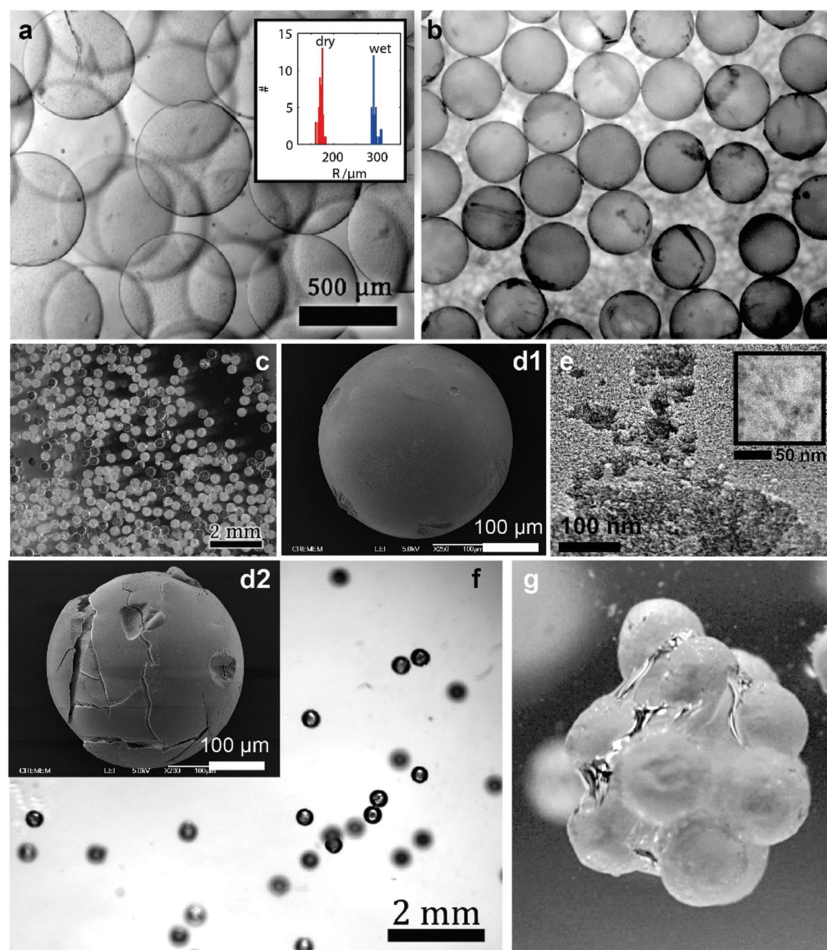


Figure 2. Calibrated porous silica particles. a) The wet particles of gelled silica are produced, collected, and dried. b) Same scale as in (a) and posttreated. Upon drying, they preserve their sphericity with 80% volume loss and a narrow size distribution (inset in (a), dispersity $\sigma/R < 3\%$). c) A large scale, darkfield view of many particles. In the same batch, a small proportion of fractured particles (scanning electron microscopy (SEM) image (d2)) co-exists with a larger proportion of smooth particles (SEM image (d1)). e) Porosity is evidenced using high resolution SEM on the surface of a particle or using high resolution transmission electron microscopy - HR-TEM - after microtome (inset in (e)), where the silica nanoparticles can be seen (dark zones, size 10–30 nm). The spherical xerogels can be dispersed in an aqueous solution ((f) a “Carbopol” aqueous gel at 0.125% solid mass fraction) only if the external surface is made hydrophilic with plasma oxidation. g) The case of native hydrophobic particles that cluster due to the lack of posttreatment, which in turn results in a poor dispersion. All acoustic measurements presented here were performed in case (f) but with a volume fraction of 20%.

was measured either at the single particle level (Figure S3 in the Supporting Information, $\rho = 0.42 \pm 0.06 \text{ g cm}^{-3}$), or on a bulk sample containing thousands of particles ($\rho \approx 0.46 \text{ g cm}^{-3}$). The two results are consistent but single particle measurements evidence a large variability of the density from particle to particle. We also recover this variability on SEM images where we indeed see that some particles are fractured (Figure 2d1,d2). Eventually, their mechanical properties were measured at the single particle level using contact experiments (Figure S4, Supporting Information) analyzed using Hertz model, yielding an effective modulus $E^* = E/(1-\nu^2)$, with E as the Young's modulus. When silanization is performed after the synthesis,

particles display a much softer modulus $E^* \approx 5\text{--}10 \text{ MPa}$ than without silanization ($E^* \approx 2000 \text{ MPa}$, see the Supporting Information). We therefore selected silanized particles for their combination of modest density and low elasticity, which makes them promising candidates for LRIs.

We measured the acoustic features of suspensions of these spherical xerogels by holding the acoustic cream directly in between an emitter and a receptor.^[8] An ultrasonic wave is transmitted through the suspension and changing the distance between the two transducers amounts to change the acoustic propagation distance, from which follows a direct measurement of the phase velocity inside the material. We kept very thin sample thicknesses (1–1.5 mm) to preserve the coherent part of the signal and to cope with the high attenuation of the suspension.

For dilute suspensions, the phase velocity (or equivalently the refractive index) remains always positive (not shown), but for the most concentrated suspension (20% volume fraction), we observe two frequency bands with negative refractive index (Figure 3a, bottom), one fairly deep with $n_{\min} \approx -2$ at low frequency and one quite shallow with $n_{\min} \approx -0.5$ at higher frequency. As detailed below, the refractive index n can be computed on the basis of material properties of the matrix and that of the inclusions, including their volume fraction, size, and dispersity. Using the accurate geometrical characterization of LRIs obtained from microscopy (Figure 2), we calculate n starting with material properties of LRIs of aerogels.^[16] While these input parameters ($c_L = 324 \text{ m s}^{-1}$ and $c_T = 197 \text{ m s}^{-1}$) do not permit to reproduce exactly our experimental results (grey curves in Figure 3b), some slight fine tuning not only opens a second band with negative index but their position is accurately described (blue curves in Figure 3b, bottom). This tuning leads to $c_L = 330 \text{ m s}^{-1}$ and $c_T = 183 \text{ m s}^{-1}$ and the resulting Poisson's ratio $\nu = 0.28$ is

consistent with the denser and less branched mesostructure of xerogels as compared to the one of aerogels ($\nu = 0.2$).^[13,16] Eventually, we recompile the Young's modulus at ultrasonic frequencies using the measured density of LRIs and obtain $E \approx 40 \text{ MPa}$, in reasonable agreement with the one measured at vanishing frequency ($E \approx 7\text{--}15 \text{ MPa}$).

We suggest that this second band of frequency with negative index originates from shear waves in the LRIs that arise from mode conversion of longitudinal waves propagating in the fluid matrix into longitudinal and transverse waves that propagate into the LRIs, and which takes place at the fluid matrix/spherical solid particles interface. In this context, the

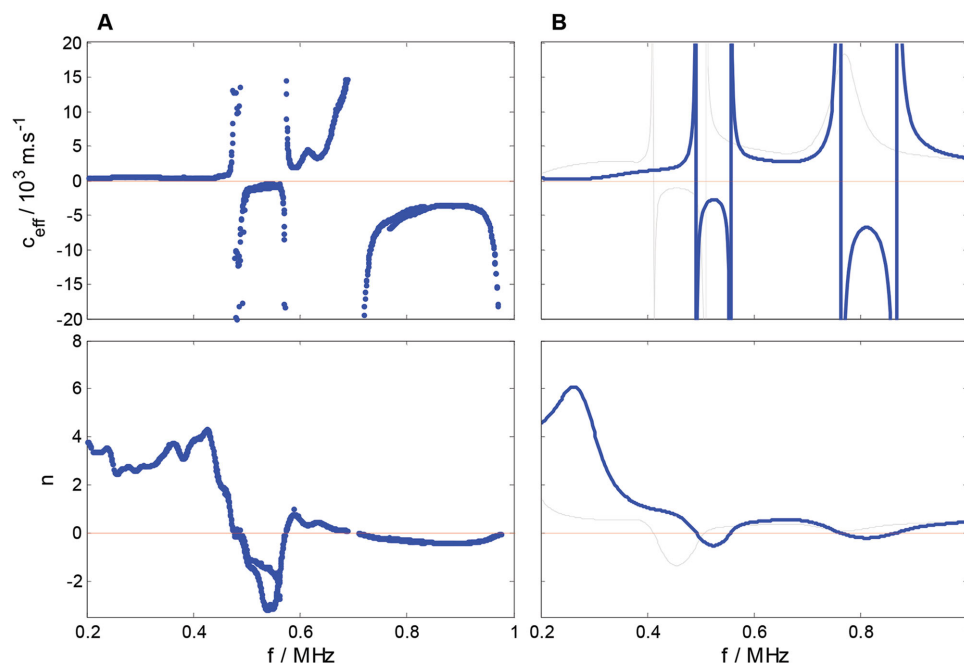


Figure 3. a) Acoustic characterization using experiments (left) and numerics (right) showing the effective phase velocity (top) and the acoustic refractive index (bottom) of a dispersion at 20% volume fraction dispersion of 180 μm -radius xerogel LRIs with 5% size dispersity. In order to match the experimental values (left), the material properties required to display two negative bands at the correct positions lead to a slow material ($c_L = 324 \text{ m s}^{-1}$ and $c_T = 197 \text{ m s}^{-1}$ with a Poisson's ratio $\nu = 0.28$). b) Grey curves were calculated using literature values for material properties of aerogels, see also Figure 4.

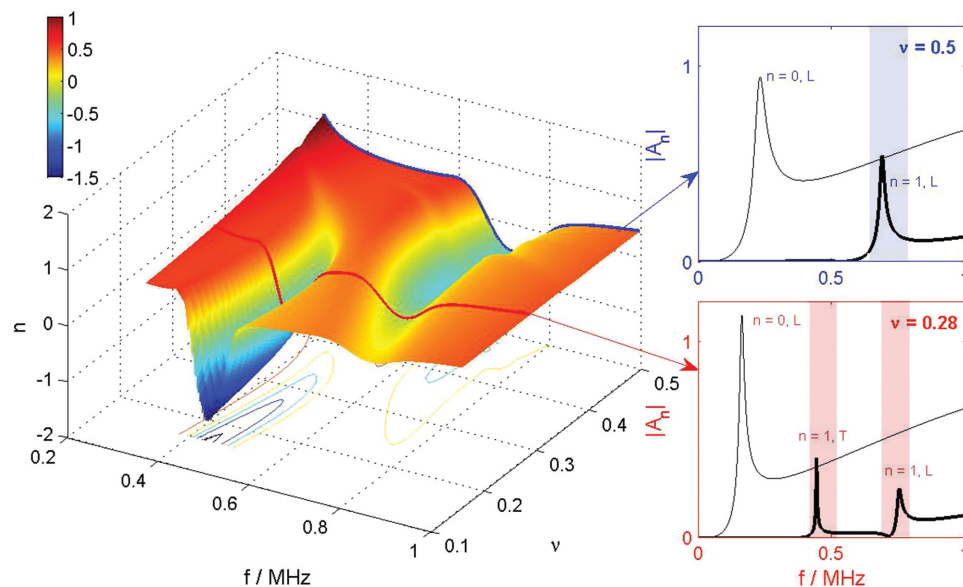


Figure 4. Left: Acoustic refractive index n of a random dispersion of locally resonant inclusions as a function of frequency f and Poisson's ratio ν of the dispersed material (for a 20% volume fraction of 180 μm -radius spherical inclusions with 5% size dispersity), and the material properties are defined as follows: the longitudinal sound celerity is that of silica aerogels $c_L = 324 \text{ m s}^{-1}$,^[14] the transverse celerity is parametrized using Poisson's ratio $c_T = f(c_L, \nu)$,^[13] for the matrix, $\rho = 1 \text{ g cm}^{-3}$ and $c_T = 1492 \text{ m s}^{-1}$. Dissipation is taken into account both for the water-based matrix (frequency-dependent attenuation coefficient $\alpha_L = 8310^{-6} \text{ Np mm}^{-1} \text{ MHz}^{-2}$), and for the LRIs (with silica aerogels attenuation coefficients: $\alpha_L = 0.12 \text{ Np mm}^{-1} \text{ MHz}^{-1}$ and $\alpha_T = 0.226 \text{ Np mm}^{-1} \text{ MHz}^{-0.5}$).^[14] Right: modal amplitudes A_n of the vibration modes of spherical inclusions for two different values of the Poisson's ratio where $n = 0$ or $n = 1$ stand for monopolar and dipolar vibration modes, respectively (the shape of which is given as movies in the Supporting Information), while L and T correspond to longitudinal and transverse waves, respectively. The vertical bands correspond to the frequency bands where the refractive index is negative.

Poisson's ratio ν which parametrizes the ratio of transverse-to-longitudinal sound celerities c_T/c_L is a good descriptor of the LRIs' material properties.^[13] Figure 4 (left) displays the real part of the acoustic refractive index n calculated within a multiple scattering Waterman–Truell scheme for a concentrated suspension of very calibrated LRIs (size dispersity 5%, volume fraction 20%), using a longitudinal sound speed typical of silica aerogels^[14,16] and a transverse sound speed tuned in the range $c_T \approx 0–220 \text{ m s}^{-1}$ via ν (in the corresponding range 0.5–0.2).^[13] While at high $\nu (\geq 0.38)$, such a dispersion displays a single band with negative index, a second band with $n < 0$ indeed occurs below this critical Poisson's ratio. The analysis of mode shape (see movies in the Supporting Information) and modal amplitudes (Figure 4, right) confirms that below the critical Poisson's ratio, a transverse dipolar resonance excited by shear waves may overlap the large frequency band where the main monopolar longitudinal resonance occurs. This coexistence of these two resonances thus appears responsible for the new frequency band of negative refractive index.

We also display in the Supporting Information (Figure S5) a parametric study of the other parameters impacting the resonance, namely the volume fraction, size and dispersity of LRIs. It turns out we can engineer both the depth and the position of the negative-index bands by the mean of material properties (ν) and the size R of the inclusions which sets the resonance frequencies ($f \approx c/R$). Oppositely, increasing the size dispersity or diminishing the volume fraction of LRIs both critically fade away the metaproperties and we acknowledge that for silicone-based LRIs,^[8] the size dispersity ($\approx 25\%$) of LRIs precluded the occurrence of two bands with $n < 0$.

As a conclusion, we regard the soft matter route as a promising toolbox for the fabrication of acoustic resonators with unprecedented properties. For instance, even if the (longitudinal) sound speed in xerogel LRIs is roughly the same as in air, their dense and solid mesostructure gives rise to significantly new acoustic features such as multiple bands with negative index, which are tunable via the size of the inclusions along with their material properties. Such an upscalable synthetic route should permit to design and engineer large scale acoustic raw metamaterials for integration and further application such as metacoatings for instance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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