Confined coherent acoustic modes in a tubular nanoporous alumina film probed by picosecond acoustics methods

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Abstract. Coherent GHz acoustic phonon dynamics in a tubular nanoporous alumina film is studied with picosecond acoustic methods. This study has allowed the determination of the out-of-plane sound velocity and the effective optical index through a time-resolved Brillouin analysis. Several acoustic eigenmodes of the tubular nanoporous alumina film were detected. These GHz eigenmodes exhibit unusual frequency-dependent long lifetimes. Their strong confinement has been explained by the presence of a thin alumina layer at the film/substrate interface which plays the role of an acoustic mirror. Finally, we show that the optical detection process of these long-living eigenmodes can be either enhanced or reduced to zero following a selection rule. In particular, we demonstrate that detection configurations exist where the coherent acoustic phonon and probe light sensitivity functions are orthogonal, leading to cancellation of the photoelastic light scattering mechanism. This has never been reported so far in the physics of the interaction of coherent acoustic phonons with light.

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1. Introduction

The understanding of elasticity and phonon transport in nanostructured materials is of prime importance for their integration into smart nanodevices [1]. Integration of such systems requires basic knowledge of their elastic properties in order to evaluate and eventually control the possible mechanical mismatch between nanostructured materials and the surrounding materials (host substrate, inserted nanoparticles, fluids, etc). These nanostructured materials are typically ordered or disordered nanoporous materials [2], colloidal supracrystals [3, 4] and multilayer nanometric films [5–8]. These nanostructured materials are used for their own original physical properties (low dielectric constant in the case of porous media [2], phononic properties in the case of nanometric superlattices [5–8] and so on) and also often used as a template and host matrix for functionalized nanoparticles with specific magnetic [9, 10] and optical [4] properties, as well as for solar energy harvesting technologies [11] and liquid confinement [12]. Some unidirectionally oriented tubular nanoporous architectures are now used even for structuring ion-channel proteins [13]. These nanostructured materials are nanocomposites in the sense that they are made of two phases at least. The main difficulty in the understanding of acoustic phonon propagation and elastic properties is related to the necessity of a precise description of the mechanical interfaces (or mechanical contacts) between the different phases of the system. Describing them is a hard task and despite a number of effective medium approaches [14, 15] as well as atomistic simulations [16], precise experimental investigations remain a necessary route. Among the most popular canonical nanostructured materials, anodized-based tubular alumina nanoporous structures have received a great deal of attention [17–20]. For anodized alumina films having a thickness of several micrometers, classical MHz transducer-based acoustic experiments are traditionally performed for the evaluation of the elastic properties [21–23]. However, for the evaluation of films with submicrometer thickness, either higher acoustic frequencies or near-field mechanical probing is required. For the latter case, nano- and micro-indentation [24] has been used to probe the elasticity of alumina nanoporous media, but it is intrinsically limited by its destructive nature. Because of this, a non-contact method using
light interaction with acoustic waves, i.e. the Brillouin light scattering (BLS) technique, became a useful and convenient method to investigate the elasticity of submicrometer films [25–27]. Therefore, BLS was recently used to study the thermal acoustic phonon spectrum in canonical tubular anodized aluminum oxide (AAO) films [28, 29]. The Brillouin zone has been explored, and both out-of-plane and in-plane phonon dispersion curves have been reconstructed and simulated.

While Brillouin spectroscopy has been widely applied so far to probe the elasticity and thermal phonon dynamics of such canonical tubular nanoporous materials [28, 29], no studies with picosecond acoustics methods have been reported to the best of our knowledge. Time-resolved picosecond acoustics methods are well known to be a powerful tool to evaluate elastic properties and coherent acoustic phonon dynamics at nanometric scales. Picosecond acoustics is based on an all-optical pump–probe method using a femtosecond laser to generate and to detect coherent acoustic phonons [30–32]. Picosecond acoustics offers a unique way to directly study in the time domain the coherent acoustic phonon propagation and to measure their lifetime [33–35]. It also offers a unique tool for nanometric depth profiling of the elasticity [36] or of the depletion layer of semiconductor junctions [37], and permits acoustic phonon confinement studies [7, 8, 38–40]. The usual way to evaluate the elastic properties of a thin homogeneous transparent film is either using the picosecond interferometric configuration (usually called time-resolved Brillouin configuration) or the measurement of the time of flight of a broadband coherent acoustic pulse within the thin film (echo configuration). Both methods provide the value of the sound speed if we know for the first and the second configuration the optical refractive index and film thickness, respectively [30, 41, 42]. In the echo configuration, in some cases, the acoustic eigenmodes of the system can also be detected by time-resolved reflectivity measurements [38, 43–47]. Measuring several eigenmode frequencies permits improvement of the precision of estimation of the sound speed in the nanometric resonator and allows in a single experiment the study of the frequency dependence of the coherent phonon lifetime. However, generating and/or detecting several eigenmodes requires a nanoresonator of good quality and/or an optimized detection scheme. In the case of a free-standing membrane which is by assumption perfectly isolated from an elastic point of view, it has recently been shown that several eigenmodes could be excited and detected by femtosecond laser action. This has permitted high-resolution sound velocity determination for submicrometric films and measurement of coherent acoustic phonon lifetimes [33, 34].

This paper presents a complete study of laser-induced coherent vibrational modes in a canonical tubular nanoporous film. By conducting time-resolved BLS experiments, the longitudinal sound speed and the effective refractive index were first determined. Then, several coherent acoustic eigenmodes of the nanoporous tubular film were successfully detected. These eigenmodes exhibit unusual long lifetimes that increase with frequency, resulting in a significant confinement effect. Finally, we demonstrate that these confined acoustic eigenmodes can or cannot be observed following a particular selection rule for the detection process. We show indeed that depending on the order of the acoustic eigenmode, the scattering of probe light by eigenmodes acoustic field can vanish or can be greatly enhanced. We demonstrate the existence of orthogonality between some acoustic eigenmodes and the probe electric field wave functions. This demonstrates that a new phenomenon of cancellation of the light scattering by acoustic phonons is possible complementary to what is already known in BLS spectroscopy where scattered intensity cancellation phenomena have already been reported, but were traditionally explained by the competition between ripple and photoelastic contributions [25–27].

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2. Experimental methods

2.1. Tubular nanoporous samples

The fabrication of the tubular nanoporous material follows the well-known anodization electrolytic process, the description and experimental details of which can be found in the literature [10, 13, 24, 48]. The typical nanostructure studied in this work is shown in the scanning electron microscope (SEM) picture in figure 1. The mean wall thickness of the tubular porous film is between 20 and 30 nm and the wall height is $H \sim 360$ nm. A dense thin alumina layer ($h \sim 60$ nm) is present at the interface between the nanoporous alumina film and the aluminum substrate. A sketch of the pump–probe experiment is shown in the inset.

2.2. Pump–probe experiments

The pump–probe technique used here consists of the optical excitation of the system by a femtosecond laser and the detection of the corresponding transient optical reflectivity using the second laser beam called the probe beam. The setup follows the classical scheme of picosecond acoustics [30–32, 49]. In the particular case of our studies, considering the fact that within the optical wavelength range of the laser excitation the tubular nanoporous material is transparent, the pump beam deposits its energy when it interacts with the aluminum opaque substrate, as is indicated by the arrow in the inset of figure 1. Owing to an ultrafast laser-induced heating of the metallic substrate, a thermoelastic stress gives rise to picosecond acoustic pulses that propagate both within the semi-infinite substrate and within the nanoporous film. The probe beam is delayed in time relative to the pump beam by using a motorized mechanical optical mirror, which permits transformation of a variation of the optical path in a time delay. The propagating laser-generated acoustic strain field leads to modifications of the refractive index and induces displacements of surfaces and interfaces, which can then be detected and monitored in the time.
domain by recording the transient reflectivity. The probe beam intensity is measured with a pin diode and the signal is processed with a lock-in amplifier. The transient reflectivity is measured over a time of 1.2 ns. The pump–probe experiments were conducted either with degenerated pump–probe configuration where both the pump and the probe have the same wavelength or by two colors of light experiments where the probe wavelength is half the wavelength of the pump. In the latter case, the probe wavelength is obtained by the second harmonic generation realized in a BBO crystal. Thanks to the tunability of the coherent Mira cavity we used, the probe beam wavelength was tuned within two ranges, namely 360–440 and 760–880 nm. Different incidence angles of the probe beam were also chosen for improving the sensitivity of the detection process, as we will discuss in detail in section 4.3.

In the particular case of the system studied in that work (figure 1), since the dense embedded alumina layer is rather thin compared to both the porous layer and the probe wavelength ($\lambda > 700$ nm), and accounting for the nearly negligible optical reflectivity coefficient at the interface between the nanoporous and dense alumina $\approx 0.08$, we can assume, as a reasonable approximation, that from the optical point of view the system can be considered as the assembly of a transparent layer deposited onto an opaque substrate. With that assumption, the transient complex optical reflectivity magnitude is $\Delta R/2R = \text{Re}(\Delta r/r)$, where \[42, 50, 51\]

\[
\frac{\Delta r}{r} = -2i k_0 \cos \theta_0 u(0) + C \left[ 2i r_{12} k_1 \cos \theta_1 (u(0) - u(H)) - \frac{i}{\cos \theta_1} \frac{\partial k_1}{\partial \eta} \int_0^H \eta(z, t) [r_{12} e^{-ik_1 \cos \theta_1 (H-z)} + e^{ik_1 \cos \theta_1 (H-z)}] \right] + \frac{i(1 - r_{12}^2)}{\cos \theta_2} \frac{\partial k_2}{\partial \eta} \int_H^\infty \eta(z, t) e^{i k_2 \cos \theta_2 z} dz
\]

with \[\text{(1)}\]

\[
C = \frac{(1 - r_{12}^2)}{(r_{01} e^{ik_1 \cos \theta_1 H} + r_{12} e^{-ik_1 \cos \theta_1 H}) (e^{ik_1 \cos \theta_1 H} + r_{01} r_{12} e^{-ik_1 \cos \theta_1 H})}
\]

where $r$ is the complex optical reflectivity coefficient of the non-perturbed system, $k_i$ is the probe wave vector in medium $i$ ($0, 1$ and $2$ are, respectively, the air, transparent layer and substrate), $\lambda$ is the probe wavelength in vacuum, $\eta(z, t)$ is the acoustic strain, $H$ is the thickness of the transparent layer and $u(z)$ is the normal mechanical displacement of the transparent layer at a position $z$. The notation $r_{ij}$ is used for the optical reflection coefficient at the interface between medium $i/j$ for an oblique incident probe beam whose polarization is perpendicular to the incidence plane:

\[
r_{ij} = \frac{n_i \cos(\theta_i) - n_j \cos(\theta_j)}{n_i \cos(\theta_i) + n_j \cos(\theta_j)}
\]

where $\theta_i$ is the incidence angle in medium $i$ defined as the angle between the probe beam and the normal of the interface between media $i$ and $j$. $\theta_j = 0$ for normal incidence.

The first term of equation (1) corresponds to the change of optical reflectivity signal phase caused by the displacement of the air/structure interface. The second term is also an interferometric contribution due to the change of the transparent layer thickness $(u(0) - u(H))$ induced by the relative interfaces displacement driven by the acoustic field (note: in the literature on Brillouin scattering by thermal phonons, this interferometric term is called the ‘ripple contribution’ \[26, 27\]). The first integral term is the photoelastic contribution due to
the scattering of the probe beam electric field by the acoustic strain $\eta(z, t)$ within the transparent layer. The last integral term accounts for the photoelastic contribution of the substrate. Like the first integral term, it describes how the electric field of the light is scattered in the substrate by the acoustic strain. According to the optical properties of the substrate, either narrowband acousto-optic detection (detection of Brillouin oscillations) or the broadband detection process (detection of short acoustic pulses) is involved when the substrate is optically transparent or opaque, respectively [52].

3. Experimental results

The transient reflectivity signal was recorded over a large time scale up to 1.2 ns. Within that range we have evidenced several frequency components. First of all, well-known Brillouin oscillations are observed in the time window 0–200 ps. These Brillouin oscillations come from the photoelastic interaction accounted for in the first integral term of equation (1). These Brillouin oscillations appear as a result of interferences between the probe light scattered by the fixed surfaces and interfaces and by the propagating acoustic waves (the sound speed $V_H$). The different reflected and scattered probe beams are depicted in the inset of figure 1, where they are labelled by numbers 1 and 3 and by number 2, respectively. In the time domain the period of the oscillations is $T_B$ [41, 42]:

$$T_B = \frac{\lambda}{2V_H n_1 \cos(\theta_1)} = \frac{\lambda}{2V_H \sqrt{n_1^2 - \sin^2(\theta_0)}}.$$  

(4)

Their frequency is $f_B = \frac{2V_H \sqrt{n_1^2 - \sin^2(\theta_0)}}{\lambda}$. These Brillouin oscillations are clearly visible within a time range between 0 and 200 ps (figures 2(a) and (b)). We can clearly observe in figures 2(a) and (b) that dividing the probe wavelength by a factor of two decreases the Brillouin period by approximately the same ratio. In that near-UV range, it is then easier to observe several oscillations than in the case of probing with red probe beam (750 nm). In addition to the Brillouin oscillations, we can detect the arrival times of the acoustic pulse at the surface of the substrate after forth and back travel within the nanoporous layer. The acoustic echo is detected at a time $t \approx 152 \pm 5$ ps (figures 2(c) and (d)) when it penetrates the metallic substrate. This detection is based on the photoelastic interaction described by the last integral term in equation (1). The time of flight of this broadband acoustic pulse is also detected through an optical interferometric contribution. When the broadband acoustic pulse penetrates within the nanoporous film, it induces a modification of the total thickness $H$ accounted for by $\sim u(H) - u(0) = \int_0^H \eta(z, t) \, dz$ in equation (1). Each time that acoustic pulse is reflected at a surface or an interface, it undergoes a modification in magnitude and/or in sign; consequently, the term $u(0) - u(H)$ is modified in time according to the time of flight of the acoustic pulse within the transparent layer. This finally leads the transient reflectivity signal to periodic jumps in magnitude [31, 41, 42, 52–54]. These jumps are well observed at $t \approx 76 \pm 5$ ps in figures 2(a) and (b), which is half the time of detection of the acoustic echo in the metallic substrate. These measurements show that at a very short time scale ($t < 20$ ps), we also detect the mechanical resonance of the thin dense alumina layer embedded between the porous thin film and the aluminum substrate. The thin alumina layer resonance is strongly damped, which makes the estimation of the ringing frequency not straightforward since only half of a period is observed. We can estimate it at $f_h \approx 100 \pm 20$ GHz (figure 2(d)). This frequency provides
Figure 2. Transient reflectivity measured with different pump–probe configurations. (a) The probe wavelength $\lambda = 750 \text{ nm}$; the external incidence angle $\theta_0 = 73^\circ$. The pump wavelength was the same as the probe one. (b) $\lambda = 400 \text{ nm}$, $\theta_0 = 41^\circ$. The pump wavelength was 800 nm. (c) $\lambda = 800 \text{ nm}$, $\theta_0 = 0^\circ$. The pump wavelength was 800 nm. (d) Derivative of the signal shown in (c). Depending on the detection configuration, we can clearly observe either the Brillouin oscillations ((a) and (b)) or the acoustic echo on curve (c) ($t_{\text{echo}} \approx 152 \text{ ps}$). The time derivative of the transient reflectivity signal shown in (c) and given in (d) evidences that on a short time scale, a high-frequency component ($\approx 100 \text{ GHz}$) exists during the first 20 ps. It corresponds to the resonance of a dense thin ($\approx 53 \text{ nm}$) alumina layer embedded between the nanoporous film and the aluminum film.

An estimation of the embedded layer thickness of $h = V_h/(2 \times 100 \text{ GHz}) \approx 52.5 \pm 10 \text{ nm}$ where $V_h = 10 500 \text{ m s}^{-1}$ is the sound speed in dense alumina.

Several additional vibration modes giving rise to complex transient reflectivity signals are also observed and can be well distinguished over a large time scale (0–1.2 ns). An example of a signal whose thermal baseline was subtracted is given in figures 3(a) and (b). The spectrum obtained thanks to a numerical FFT given in figure 3(c) shows that we are able to distinguish several modes. The detected frequencies are about 3, 10, 16, 24, 29, 48 and 76 GHz (table 1). Preliminary estimates show that these frequencies are acoustic eigenmodes of a layer bonded on a rigid substrate and their frequencies follow the $f = (2n - 1)V_H/4H$ ($n = 1, 2, \ldots$) sequence. Up to 12 modes have been detected. This statement will be confirmed in section 4.2 on the basis of a more detailed model. Furthermore, two important peculiar properties are observed.
Figure 3. (a) Time derivative of the transient reflectivity signal over a large time scale (probe wavelength $\lambda = 750$ nm and external incidence angle $\theta_0 = 21^\circ$). The baseline has been removed for clarity of presentation of the vibratory component. For $t < 200$ ps, the Brillouin frequency (about 17 GHz) is the main component. At longer time scale, several additional components are detected. (b) Zoom of the time scale 400–1200 ps. The dashed line depicts the first acoustic vibration eigenmode of the nanoporous film. (c) Fast Fourier transform (FFT) of the signal shown in figure 3. The modes at 48 and 76 GHz are magnified by a factor of 2. $n$ is the eigenmode number. (Inset) FFT obtained for different detection configurations. Red curve: $\lambda = 750$ nm, $\theta_0 = 41^\circ$; blue curve: $\lambda = 400$ nm, $\theta_0 = 73^\circ$. The FFT plots were normalized in magnitude to the maximum peak for clarity.
Table 1. Experimental and theoretical values of the 12 first eigenmodes frequencies $f_n$ of tubular nanoporous alumina. Depending on the detection configuration some eigenmodes are detected or not (columns 1–3). The experimental and theoretical imaginary parts of the eigenmode frequencies given in parentheses in the first and last columns are in good agreement.

| Detection 1 | Detection 2 | Detection 3 | Numerical (GHz) |
|-------------|-------------|-------------|-----------------|
| Probe wavelength (nm) | 750 | 735 | 400 |
| External angle ($\theta$) (deg) | 21 | 34 | 73 |
| Eigenmode index $n = 1$ | 2.9 | 2.9 | 2.94 | 3.74 (+i1.27) |
| Eigenmode index $n = 2$ | 11.3 (+i1.22) | 11 (+i0.59) | 11.5 | 10.76 (+i0.59) |
| Eigenmode index $n = 3$ | – | – | 16.9 | 17.5 (+i0.35) |
| Eigenmode index $n = 4$ | 24.1 (+i0.23) | 23.9 (+i0.31) | 24.5 | 24.2 (+i0.23) |
| Eigenmode index $n = 5$ | 29.9 (+i0.21) | 30.3 (+i0.19) | 30 | 30.8 (+i0.19) |
| Eigenmode index $n = 6$ | – | – | – | 37.5 (+i0.17) |
| Eigenmode index $n = 7$ | – | – | – | 44.2 (+i0.17) |
| Eigenmode index $n = 8$ | 48 (+i0.21) | 48.5 (+i1.3) | – | 50.8 (+i0.19) |
| Eigenmode index $n = 9$ | – | – | – | 56.2 (+i0.25) |
| Eigenmode index $n = 10$ | – | – | – | 63 (+i0.37) |
| Eigenmode index $n = 11$ | – | – | – | 69.5 (+i0.64) |
| Eigenmode index $n = 12$ | 76 (+i0.85) | 76 (+i0.99) | – | 75.7 (+i1.41) |

Firstly, it appears that the spectral weights of these modes strikingly depend on the configuration of the detection (probe wavelength and incidence angle) with sometimes a cancellation of their detection, like for the mode at $\approx 16$ GHz. Secondly, the imaginary part ($\text{Im}(f_n)$) of these eigenmodes (given in parentheses in table 1) exhibits unusual behavior since it decreases with frequency up to the mode at $\approx 30$ GHz and shows an increase for the higher frequency modes (76 GHz). This means that the lifetime $\tau = (2\pi \text{Im}(f_n))^{-1}$ exhibits non-monotonic behavior revealing frequency-selective acoustic mode confinement. This imaginary part was estimated after having fitted each peak according to a Lorentzian function convoluted with a cardinal sinus function taking into account the finite size of our time window of measurement. Experimental peaks of vibrational modes are superimposed in figure 5(a) where we clearly observe the non-monotonic frequency dependence of the peak width revealing the dependence of the acoustic confinement on mode frequency. These two original properties will be explained in sections 4.2 and 4.3 after discussing time-resolved BLS in section 4.1.

4. Elastic properties, acoustic mode confinement and detection selection rules

4.1. Time-resolved Brillouin light scattering

In this subsection we make use of a parametric study of the Brillouin period (equation (4)) to extract the sound speed $V_H$ and the refractive index $n_1$ of the tubular nanoporous film. In order to determine these constants, two series of measurements have been carried out. In the first configuration, the external incidence angle $\theta_0$ was fixed and the laser probe wavelength $\lambda$ was tuned in the ranges (360–440 nm) and (720–880 nm). In the second configuration, the
The Brillouin frequency $f_B = 1/T_B$ versus the probe beam light wave vector.

Figure 4. The Brillouin frequency $f_B = 1/T_B$ versus the probe beam light wave vector.

probe wavelength $\lambda$ was fixed and the external incidence angle was changed to cover the $[0–73^\circ]$ range. The treatment of these two series of measurements of the Brillouin frequency, $f_B$, was then accomplished according to a double mean least-squares procedure assuming that theoretically $f_B$ depends linearly on $k_0 = 2\pi/\lambda$ ($f_B = V_H k_0 \sqrt{n_1^2 - \sin^2(\theta_0)/\pi}$). An example of the fitted Brillouin frequency is presented in figure 4. In this data processing, we assumed that the optical refractive index of the transparent layer is constant over 360–880 nm. Actually, in this range of wavelengths, the Al$_2$O$_3$ optical index varies very slightly, $\Delta n/n \approx 1.5\%$ [55]. We obtained then an estimation of the sound velocity $V_H = 5040 \pm 150$ m s$^{-1}$ and an optical index of $n = 1.51 \pm 0.05$. Furthermore, taking into account the time of flight of the acoustic pulse within the nanoporous layer and the dense alumina layer, we obtain the porous alumina layer thickness $H = V_H^2 \times (t_{echo} - 1/f_h) \approx 357 \pm 10$ nm, consistent with what is expected from the preparation processes. Moreover, using the Maxwell–Garnett model [56] for the effective optical index $n_1$ of our tubular nanoporous alumina film and considering the refractive index of the dense alumina ($n_{Al_2O_3} = 1.76$), the tubular nanoporous film porosity $\phi \approx 0.43$ is obtained. An effective elastic modulus of $\sim 60$ GPa is then deduced, in good agreement with the value of $\approx 100$ GPa obtained by nanoindentation [24]. Our estimates are also in excellent agreement with the values obtained by Sato et al [28] where a sound speed of 5040 m s$^{-1}$ was measured in native AAO exhibiting a porosity of $\phi = 0.32$ (see the supplementary material in [28]).

4.2. Confined acoustic eigenmodes

In order to clearly establish that the discrete modes reported in figure 3(c) are acoustic eigenmodes of the nanoporous layer, we have analytically determined the eigenmodes’ complex cyclic frequencies $\omega$ of the structure composed of two layers on the substrate presented in the inset of figure 1. For that, the solutions of the equations of mechanical motion, satisfying the boundary conditions at free surface and at interfaces, were found. Assuming the displacements and stress continuity at interfaces, the eigenmode equation is

$$N_{12} \tan \left( \omega \frac{H}{V_H} \right) = \frac{1 + iN_{23} \tan \left( \omega \frac{h}{V_H} \right)}{\tan \left( \omega \frac{h}{V_H} \right) - iN_{23}},$$

(5)
$N_{ij}$ is the ratio of acoustic impedances of media $i$ and $j$ ($N_{ij} = N_i/N_j$), where $i = 0, 1, 2$ and $3$ is attributed to the air, nanoporous film, dense embedded alumina layer and aluminum substrate, respectively. We recall that $H$ and $V_H$ ($h$ and $V_h$) are the thickness and sound velocity in the nanoporous layer (dense alumina layer). We numerically adjusted each real part of the frequency of the experimental spectrum according to that model and the best correspondence was found for $V_H = 4880 \pm 100 \text{ m s}^{-1}$ and $H = 362 \pm 8 \text{ nm}$. The physical parameters of aluminum and alumina are given in footnote 2. These theoretical frequencies are summarized in the last column of table 1. In the numerical adjustment we had fixed $h = 60 \text{ nm}$. This set of values is consistent with the values obtained in section 4.1 confirming the physical origin of the discrete detected frequencies. It should be noted that the value of $h$ does not influence so much the real part of the theoretical value of the eigenmodes frequency but strongly influences the imaginary part. This $h$ value is refined in the following through the study of the lifetime of the eigenmodes.

As especially pointed out by the first column of table 1, the experimental results show that the lifetime (inverse of the imaginary part of the eigenmode frequency) is a non-monotonic function of the frequency. More spectacular, a minimum (maximum) of the imaginary part of the lifetime is reported. This shows that some acoustic eigenmodes, in particular the modes with the values obtained in section 4.1 confirming the physical origin of the discrete detected phenomena (acoustic mirror effect), to the optimum acoustic reflection of an incident acoustic wave having a wavelength $\lambda$. The theoretical lifetime, determined as $\tau = 1/(2 \log(|R|) f_H)$, is a periodic function of $f$ with the period $f_h$. The maximum of the lifetime is obtained when the incident acoustic frequency follows the sequence $f = (2n-1) f_h/2$ ($n = 1, 2, \ldots$) corresponding, through a constructive interference phenomenon (acoustic mirror effect), to the optimum acoustic reflection of an incident acoustic wave having a wavelength $\lambda = 4h/(2n-1)$. We have numerically adjusted that theoretical lifetime of each $n$th eigenmode as shown in figure 5(b), where experimental results are superimposed on the theoretical ones. Reasonable agreement is found. In that adjustment only the thin layer thicknesses $h$ were adjusted. The best value we found is $h = 65 \pm 5 \text{ nm}$. The physical parameters used for that calculation are given in footnote 2.

2 Longitudinal sound speeds of the aluminum substrate, of the dense embedded layer and of the nanoporous film are: $V_3 = 5700 \text{ m s}^{-1}$, $V_h = 10520 \text{ m s}^{-1}$ and $V_H = 4880 \text{ m s}^{-1}$. The corresponding densities are $2600 \text{ kg m}^{-3}$, $3900 \text{ kg m}^{-3}$ and $(1-\phi) \times 3900 = 2220 \text{ kg m}^{-3}$, respectively, with $\phi = 0.47$. 
Figure 5. (a) Comparison of the normalized experimental eigenmode peak widths. The non-monotonic dependence of the peak width on frequency is clearly seen. (b) Theoretical (broken line) and experimental lifetime (triangles and diamonds corresponding to different experimental configurations described in table 1) of each $n$th confined eigenmode versus its frequency $f_n = (2n - 1)f_H$ for an alumina layer thickness of $h = 62$ nm. The theoretical lifetime is calculated either from equation (6) or from the approximated imaginary part for the eigenmode frequency equation (A.3).

The model of confined acoustic waves provides confident explanations for the origin of the frequency-dependent unusual long lifetime of eigenmodes. Nevertheless, that model cannot explain the striking features of the detection process, i.e. our failure to detect some of the eigenmodes ($n = 3, 6, 7$) while their theoretical lifetime is of the same order as that of the mode $n = 4$ ($f_4 \approx 24$ GHz) for example. This detection effect, which has never been reported so far, is due to a peculiar detection process described in the following.

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4.3. Selection rules for the optical detection of the confined acoustic eigenmodes

To account for the drastic difference in the detected spectral weight of eigenmodes, a complete numerical calculation of the theoretical transient reflectivity has been carried out. Following equation (1), both the photoelastic and interferometric (or ripple) contributions of each $n$th eigenmode can be evaluated as a function of the external incidence angle $\theta_0$ and for different probe wavelengths $\lambda$. According to section 4.2, we can describe the eigenmodes acoustic strain field simply as $\eta(z, t) = A(n) \sin(2n + 1) \frac{\partial}{\partial n} \sin(\omega t)$, where $A(n)$ is the magnitude of the acoustic strain of the $n$th eigenmode. The photoelastic contribution of the $n$th eigenmode to the transient reflectivity becomes then $(\Delta R/2R)_{\text{photo}} = \text{Re}(\Delta r/r)_{\text{photo}}$, where

$$
\left( \frac{\Delta r}{r} \right)_{\text{photo}} = -\frac{iC \sin(\omega t)}{\cos \theta_0} \frac{\partial k_1}{\partial \eta} \int_0^H A(n) \sin \left[ (2n - 1) \frac{2\pi z}{4H} \right] \times \left[ r_{12} e^{-ik_1 \cos \theta_1(H-z)} + e^{-ik_1 \cos \theta_1(H-z)} \right]^2 \sin(\omega t) dz
$$

Here we have introduced the notation $f(z)$ for the so-called ‘sensitivity function’ of photoacoustic detection in the transparent film [30].

The interferometric contribution was evaluated according to

$$
\left( \frac{\Delta r}{r} \right)_{\text{Interf}} = -2iCr_{12}k_1 \cos \theta_1 (u(0) - u(H))
$$

$$
= 2iCr_{12}k_1 \cos(\theta_1) A(n) \frac{4H}{2\pi(2n - 1)} \sin(\omega t).
$$

Since the photoelastic coefficient of the nanoporous film is unknown, only the normalized term $(\Delta r/r_0)_{\text{photo}}/(\Delta k_1)$ was first estimated assuming $\frac{\partial k_1}{\partial \eta}$ to be real. We took $n_2 = 2 + i8$ for the refractive index of the aluminum substrate at a probe wavelength $\lambda = 750$ nm [57]. We considered $A(n) = 1$ as a reasonable approximation in our frequency range of interest.

The results shown in figure 6(a) underline that the photoelastic contribution exhibits a strong incidence angle dependence compared to the interferometric contribution and can vary a lot in magnitude from one eigenmode to another. In particular, these results indicate that for some values of the external angle (typically 15–20°), the photoelastic term vanishes for the eigenmode $n = 3$, while it exhibits a maximum for the eigenmode $n = 4$. In contrast, the interferometric contribution (figure 6(b)) is much the same for these neighboring modes $n = 3$ and 4. Consequently, these calculations show that the detection process through the interferometric mechanism cannot explain the dramatic variation of detected intensity between neighboring eigenmodes $n = 3$ and 4. We claim then that our experimental observation of the inhibition of some particular modes ($n = 3$) is actually driven by the vanishing photoelastic term, which appears to be the most important contribution in the detection process. One of the original conclusions of this analysis is that there are detection configurations where the photoelastic contribution cancels. This means that the acoustic strain field of that eigenmode is orthogonal to the sensitivity function of the probe light. This is well illustrated if we

3 In these calculations we have considered that each of eigenmodes has the same spectral weight ($A(n) = 1$), which is reasonable for the pretty low frequency range of investigation (0–80 GHz) considering that the spectrum of the photogenerated coherent acoustic phonons is broad in opaque materials such as aluminum.

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superimpose the acoustic eigenmode acoustic strain field and the probe light electric field sensitivity function (figure 7). In particular, we clearly observe their orthogonality for the eigenmode \( n = 3 \). They have the same periodicity in space but are \( \sim \pi/2 \) phase shifted. Additional calculations, not shown here, performed for a probe wavelength of 400 nm show that the eigenmode \( n = 3 \) is no more vanishing in that detection configuration consistently with the experimental observation (see the third column of table 1 and the inset of figure 3(c)).

In order to support our claim, it remains important to discuss another possible cause of inhibition. Cancellation of the signal of light scattering due to the mutual compensation of photoelastic contributions from a transparent film and the host substrate has already been reported [27]. But in that case it is known that such a cancellation effect occurs following a parity law where inhibition concerns either the odd or the even eigenmodes [27]. This is
Figure 7. (Left) Plot of the acoustic field of each eigenmode and the probe electric field for an external incident angle of 15°. The orthogonality of both fields clearly appears for the eigenmode $n = 3$, while they are pretty much in phase for $n = 4$. The corresponding theoretical photoelastic contribution to transient reflectivity signal of each eigenmode is given in the right panel.

actually not the case we report in our experimental observation. As a consequence, our detection process analysis supports our initial claim of the existence of a possible orthogonality between the probe light ‘sensitivity function’ and the acoustic strain field. This defines the selection rule for inhibition/cancellation of the photoelastic detection that has never been evidenced until now in the physics of interaction of coherent acoustic modes with light. This original mechanism of the signal detection based on the coherence (orthogonality) of the acoustic field and optical sensitivity function is able to selectively activate (suppress) the light scattering by a given confined acoustic eigenmode. It should be noted that it has recently been demonstrated [58] that it is possible to maximize the overlap integral between the standing acoustic field and the optical ‘sensitivity function’ by spatial tuning of both the photo-generated acoustic field and the probe optical field. In [58], the acoustic strain field is tuned by its photo-generation process and design of the acoustic resonator in addition to tuning the ‘sensitivity function’ of the confined probe optical field by appropriately choosing the optical wavelength and the angle of probe incidence and by designing the multilayered material for optical confinement. The work [58] does not discuss the opportunities to enhance, by modifying the optical probe ‘sensitivity function’ of weakly confined probe electromagnetic fields, the detection of an arbitrary confined acoustic phonon, whose strain is not tuned by its generation process to the ‘sensitivity function’ of the
optical field. Our research results are related to a different experimental situation, where we demonstrated that the electromagnetic probe field can be tuned to either enhance or diminish the Brillouin scattering from the confined phonons, which are not specially created to fit the probe electromagnetic field ‘sensitivity function’.

5. Conclusions

In this experimental and theoretical work, coherent GHz acoustic phonon dynamics in submicrometric tubular nanoporous alumina was studied with picosecond acoustics methods. Time-resolved BLS (picosecond interferometry), time of flight measurements of acoustic phonons and the generation and detection of acoustic vibration eigenmodes of the nanoporous film are three coupled techniques that we have used to determine the sound velocity in tubular nanoporous alumina. We have demonstrated that it is possible to excite and detect up to 12 confined acoustic eigenmodes of the tubular nanoporous film. We have reported that these confined acoustic eigenmodes exhibit an unusual long lifetime that can be satisfactorily explained by an acoustic mirror effect due to the existence of a thin dense alumina layer embedded between a tubular nanoporous alumina film and the aluminum substrate. Finally, we demonstrate that our failure to detect some particular eigenmodes through the photoelastic effect is due to the orthogonality of the acoustic standing-wave function and the probe beam electric field sensitivity function. By choosing a proper detection configuration, it is possible to either enhance or cancel the detection of particular confined acoustic modes.

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Appendix

For the description of the quasi-equidistant weakly attenuated acoustic modes observed in experiments, the approximate analytical solutions of equation (5) can be derived by the method of successive approximations. For the convenience of the subsequent analysis, we rewrite this equation, by introducing the characteristic frequencies $f_H = V_H/4H$ and $f_h = V_h/2h$ of the quarter-wavelength oscillations of the porous layer and of the thin half-wavelength oscillations of the alumina layer, respectively,

$$N_{12} \tan \left( \frac{\pi f}{2 f_H} \right) = \frac{1 + iN_{23} \tan \left( \frac{\pi f}{f_H} \right)}{\tan \left( \frac{\pi f}{f_h} \right) - iN_{23}},$$

(A.1)

where $f$ is the complex resonance frequency of the vibrations. We search for the solution of equation (A.1) in the form $f \approx (2n - 1)f_H + \Delta f' + i\Delta f''$ with $n = 1, 2, \ldots$, by assuming that corrections to the quarter-wavelength resonances of the porous layer, caused by the fact that the reflection of the acoustic waves at the interface of the porous layer with the structure composed of a thin aluminium layer on the substrate is not perfect, are small ($(\pi/2)(|\Delta f',''|/f_H) \ll 1)$. 

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The first-order contributions to the real and imaginary parts of the resonance frequency in terms of these small parameters are

\[
\frac{\pi}{2} \Delta f' = \frac{N_{12} (N_{23}^2 - 1) \tan \left( \pi (2n - 1) \frac{f_h}{f_h} \right)}{1 + N_{23}^2 \tan^2 \left( \pi (2n - 1) \frac{f_h}{f_h} \right)}, \tag{A.2}
\]

\[
\frac{\pi}{2} \Delta f'' = \frac{N_{12} N_{23} \left( 1 + \tan^2 \left( \pi (2n - 1) \frac{f_h}{f_h} \right) \right)}{1 + N_{23}^2 \tan^2 \left( \pi (2n - 1) \frac{f_h}{f_h} \right)}. \tag{A.3}
\]

The analysis of the approximate solutions (A.2) and (A.3) demonstrates that they are very precise under the conditions \(N_{23}^2 \gg 1\) and \(N_{12} N_{23} \ll 1\). In our system the first condition holds reasonably well (\(N_{23}^2 \approx 5–6\)), but the second is not satisfied (\(N_{12} N_{23} \approx 0.5–0.6\)). However, the approximation (A.2) and (A.3) appears to be satisfactory for the experimentally observed resonances in our system because of the inequality \(N_{23} > 1\) and the specific condition \(f_H \approx 0.1 f_h \ll f_h\), which holds due to the extremely small thickness of the alumina layer. Analysis demonstrates that the deviation of the approximate solution equations (A.2) and (A.3) from the precise solution of equation (A.1) is most important for the first (fundamental, \(n = 1\)) mode, but diminishes with the increasing order \(n\) of the observed resonance oscillations. In particular, equation (A.3) provides an analytical prediction for the diminishing of \(\Delta f''\), i.e. for increasing lifetime, of the resonance modes with increasing \(n\) as far as the tangent function in equation (A.3) grows with \(n\). To obtain even better insight into the physics of the long-living higher-order modes, we have derived the reflection coefficient \(R\) of the displacement acoustic waves at the interface between the porous layer and the structure composed of an aluminum layer on a semi-infinite substrate (equation (6)). The analysis of equation (6) given in section 4.2 shows that the modulus of the reflection coefficient, which controls the energy losses of the acoustic waves confined in the porous layer by the emission of the acoustic waves into the substrate, varies in phase with the square of the tangent function, i.e. it grows when the modulus of the tangent grows and diminishes when the latter diminishes, as long as the condition \((R_{12}/R_{23}) < 0\) holds. This condition holds in our system and, consequently, continuous growth of the lifetime of the acoustic modes could be expected for \(0 < f < f_h/2 \approx 50\) GHz, in complete agreement with our experimental observations. It is worth noting here that the finite lifetime \((2\pi \Delta f'')^{-1}\) of the acoustic modes, caused by the energy leakage to the substrate mediated by the thin alumina layer, is related to the reflection coefficient in equation (6) by \((\pi/2)(\Delta f''/f_H) = (1/2) \ln(1/|R|))\), i.e. when the modulus of the reflection coefficient increases, the lifetime (confinement) of the acoustic mode increases.

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