Anisotropic propagation and confinement of high frequency phonons in nanocomposites

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We show that self-ordered anodic aluminum oxide containing hexagonal arrays of cylindrical nanopores with submicron periodicity is a versatile model system for the exploration of rich phononic phenomena at gigahertz frequencies, which are intimately linked to fluids located in the nanopores and their interactions with the pore walls. Using high-resolution Brillouin spectroscopy we report the first realization of directional flow of elastic energy parallel and perpendicular to the pore axes, phonon localization, and tunability of the phononic band structure. © 2009 American Institute of Physics. [DOI: 10.1063/1.3096972]

Recently, there has been considerable interest in phononic materials exhibiting periodic variations in their density and elastic properties that modify the propagation of sound waves, and band gaps prohibiting sound propagation for specific wavelengths commensurate with their lattice constant may occur. Their design involves engineering of both the band gap frequency region and the flow of elastic energy outside the band gap. The phononic band diagram of periodic composite media can be engineered by the solid or liquid nature of the components, the contrast between their densities and elastic constants, their volume fractions, as well as by the symmetry and morphology of the lattice they constitute. Up to now, research has predominantly been focused on the search for absolute band gaps in solid structures with lattice constants in the millimeter range. Configurations based on arrays of aligned cylindrical channels filled with liquids in a rigid matrix have remained essentially unexplored. Only few attempts to adapt concepts for functional phononic band gap structures to the gigahertz frequency range have been reported, despite the potential of such systems for a plethora of applications. A peculiar advantage of hypersonic phononic systems is the possibility to engineer interactions between phonons and visible wavelength photons, thus enabling the design of miniaturized acousto-optical devices. Here we demonstrate, using anodic aluminium oxide (AAO)-based nanocomposites as model systems, directional flow of elastic energy, phonon localization, and tunability of the phononic band structure. Moreover, a new phononic branch observed in the fluid-filled AAO seems to relate to the presence of thin interphases with enhanced elasticity.

AAO contains hexagonal arrays of aligned nanopores [see Fig. S1 (Ref. 23)] and offers unique advantages as a material platform for the investigation of sound propagation in the gigahertz frequency range: (i) Its lattice parameters perfectly match the requirements for manipulation of sound propagation in the hypersonic range; (ii) its exceptionally high longitudinal (c_{lAAO}=7300 m/s) and transverse (c_{tAAO}=3750 m/s) sound velocities (cf. supplemental material), as compared to air (c_{l}=340 m/s) or soft materials deposited into the nanopores (c_{l} typically of the order of 1500 m/s), result in composites with large elastic contrast between their constituents; and (iii) hybrid systems with tailored phononic properties are accessible by the proper choice of the infiltrated component. Within certain limitations, the pore diameter d, the lattice constant a, and the porosity p (portion of pore volume of the overall membrane volume) are adjustable by the conditions under which the AAO is prepared.

The elastic wave propagation in AAO along high symmetry directions of the two-dimensional lattice constituted by the nanopores and the liquids located in the nanopores was simulated by means of numerical band structure calculations using the finite difference time domain (FDTD) method. We employed a simple model in which homogeneous liquid poly(dimethyl siloxane) (PDMS) cylinders were in contact with the pore walls of the AAO scaffold; alumina and PDMS were assumed to be elastically isotropic media. Thus, band structures (frequency f versus wave vector q) consisting of branches (hereafter denoted by numbers) are obtained. The sound phase velocity associated with modes (hereafter denoted by letters) corresponds to the slope of the branches at low wave vectors. Figures 1(a) and 1(b) show the band structure of air-filled AAO (p=32%, solid black symbols) and PDMS-filled AAO (p=32%) (open red symbols) for wave propagation perpendicular to the nanopores [Fig. 1(a)], denoted by in-plane wave vectors [q_{l} in Fig. 2(a)] and wave propagation parallel to the nanopores [Fig. 1(b)], denoted by out-of-plane wave vectors [q_{l} in Fig. 2(b)].

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The two lowest in-plane branches starting at the $\Gamma$ point are longitudinal and transverse acoustic. Infiltrating AAO with PDMS leads to a significant decrease in $c_l = 2\pi f / q_l$ from 4940 to 4730 m/s, whereas both acoustic branches bend due to their interaction with a flat band at around 8.5 GHz, corresponding to a confined mode inside the PDMS cylinders. Increasing $p$ to 65% [see Fig. S2 (Ref. 23)] results in a strong decrease in $c_l$ and bending at a lower frequency. Mode $A'$ is a longitudinal mode in air-filled AAO that propagates only through the AAO scaffold but not through the empty nanopores, whereas in PDMS-filled AAO, mode A with the same wave vector $q_l = 0.004$ nm$^{-1}$ is spread over both the AAO scaffold and the PDMS located in the nanopores [Fig. 1(c)]. Since the latter mode senses the PDMS, it propagates slower than mode $A'$ in air-filled AAO. Remarkably, mode B with $q_l = 0.03$ nm$^{-1}$, which is a characteristic of the flat band interacting with the propagating acoustic branches, is well confined inside the PDMS cylinders.

For the out-of-plane propagation, air-filled AAO [Fig. 1(b), black symbols] exhibits two acoustic branches with mainly longitudinal and transverse polarizations, whose velocities are lower than but close to those of bulk alumina. However, the dispersion behavior drastically changes when the nanopores contain PDMS. The lowest acoustic branch (3) [Fig. 1(b)] which is essentially longitudinal, penetrates only slightly into the AAO scaffold and is largely confined to the PDMS cylinders [see Fig. 1(c) for the mode denoted by C]. Its velocity (about 900 m/s) is close to but slower than the sound velocity ($1050 \pm 20$ m/s) in bulk PDMS. Strikingly, branch (3) is absent in air-filled AAO. The highest acoustic branch (5) ($c_l = 6550$ m/s) is polarized parallel (along the $z$-direction) to the nanopores. Moreover, branch (5) is essentially confined to the AAO, as indicated by the biased distribution of the elastic field belonging to mode $A''$ in Fig. 1(c). The spatial distribution of the elastic field belonging to mode A on branch (1) in Fig. 1(a) and to mode $A''$ on branch (5) in Fig. 1(b) are distinctly different, thus rationalizing the much lower slope (4730 m/s) of the in-plane longitudinal phonon (1) that propagates also through the liquid PDMS.

Low molecular mass PDMS ($M_w = 970$ g/mol) in the proximity of solid surfaces is prone to surface-induced ordering, resulting in the formation of a layered PDMS interphase with reduced mobility. Thus, FDTD calculations were performed using a refined model in which the presence of a 5 nm thick solid PDMS interphase with a finite transverse sound velocity $c_t = 100$ m/s was assumed. As seen in Fig. 1(a) (blue points), this results in the appearance of a new flat branch (2) at 5.1 GHz, whereas branch (1) and its bending retain essentially the same characteristics as for the fully liquid PDMS cylinders. As shown for mode D [Fig. 1(d)], the displacement $U_x^2 + U_y^2$ of branch (2) with mixed polarization is essentially confined to the PDMS interphase. The frequency of this branch depends on the thickness and the transverse sound velocity of the PDMS interphase.
The most intriguing predictions of the theoretical dispersion relations of AAO are as follows: (a) The anisotropic elastic properties perpendicular and parallel to the nanopores manifested by (i) the softening (decrease in $c_l$) and bending of the main acoustic branch (1), respectively, at low and high wave vectors for in-plane sound propagation and (ii) the biased effective medium behavior of branch (5) for out-of-plane sound propagation in PDMS-filled AAO; (b) The distinct impact of the material located in the nanopores on the lowest acoustic branch (3) for the out-of-plane sound propagation; and (c) the interphase-sensitive branch (2) that is only active in the presence of a thin solidified PDMS interphase in the proximity of the pore walls.

Brillouin spectroscopy (BLS) is based on inelastic scattering of the incident laser beam by thermally excited phonons propagating through a medium along specific directions determined by the scattering geometry [Figs. 2(a) and 2(b)]. Figure 2(c) shows BLS spectra for the in-plane wave propagation in PDMS-filled AAO ($p=65\%$) and Fig. 2(d) presents BLS spectra for the out-of-plane phonon propagation in AAO with three different porosities at a similar $q_\perp$ value. At low $q_\perp$, the spectra display an effective medium behavior with a doublet at $\pm c_l q_\perp/2\pi$, and the sound velocity $c_l$ of the acoustic branch (1) is found to increase with decreasing porosity in agreement with the FDTD calculations [see Table S1 Ref. 23]. At $q_\perp \approx 0.013 \text{ nm}^{-1}$, the spectra belonging to the two highest $q_\perp$ values reveal bending of branch (1) and remarkably indicate the presence of a second lower-frequency branch (2) apparently corresponding to the interphase-sensitive branch (2) seen in Fig. 1(a). Notably, for air-filled AAO, we observe only one longitudinal and one transverse phonon with effective medium sound velocities (not shown) in agreement with Fig. 1(a).

Figure 3 presents exemplary dispersion curves $\omega(q_\perp)$ in air-filled AAO [branch (1), solid lines] and in PDMS-filled AAO [branches (1) and (2), symbols] with a porosity of 32%. In air-filled AAO, the slope of the solid lines yields the sound velocity in the effective composite medium; within an error of 2%, $c_l$ amounts to 6120, 5040, and 3510 m/s, respectively for porosities of 11%, 32%, and 65% [Table S1 (Ref. 23)]. In the PDMS-filled AAO, $c_l$ obtained from the linear dispersion of phonon (1) at low $q_\perp$ values (dashed lines) is systematically lower than in air-filled AAO [see Fig. S3 (Ref. 23)]. Also the disparity increases with porosity, reaching about 800 m/s for $p=65\%$.

The theory for all studied phononic structures captures quantitatively the in-plane elastic velocities [see Table S1 (Ref. 23)]. The softening of branch (1) is an unexpected finding since $c_{PDMS} \approx 3c_{air}$, which is, however, nicely rationalized by the different displacement distributions of modes A and A seen in Fig. 1(e); phonons travel slower through PDMS-filled AAO than through air-filled AAO. The bending of the acoustic branch (1) is only observed when the nanopores contain PDMS. Moreover, in air-filled AAO, its frequency decreases with porosity. This second unanticipated observation is represented by mode B in the theoretical band diagrams [Figs. 1(a) and Fig. S2 (Ref. 23)]. The frequency of this band is very sensitive to the choice of the sound velocity $c_{PDMS}$ in the PDMS cylinders since this mode is predominantly confined to the PDMS cylinders in the nanopores [mode B in Fig. 1(c)]. To account for the experimental effective velocities as well the bending frequency of branch (1), the value of $c_{PDMS}$ has to be about 20% lower than in bulk PDMS. This value for in-plane propagation characterizes the physical state of the PDMS in nanopores.

A strong evidence of the presence of a PDMS interphase at the pore walls is the additional in-plane branch (2) with clearly nonacoustic behavior observed in PDMS-filled AAO for any $d$ value between 35 and 85 nm [Fig. S3 (Ref. 23)]. The almost flat branch (2) shown in Fig. 3 appears in the computed band diagrams in Fig. 1 only if the presence of a thin solid PDMS interphase is used, whereas this branch is absent if the simulations are based on models assuming the presence of homogeneous liquid PDMS cylinders in the nanopores. An obvious consequence is the support of shear waves by the solidlike PDMS interphase,26 which was included in the calculations through an adjusted $c_l$ and fixed interphase thickness.26 As seen in Fig. 1, the theory predicts the presence of a flat branch (2) (Fig. 3) and captures its frequency which increases with $c_l$ and decreases with thickness. The assignment of the new branch (2) suggests that gigahertz phononics could serve as a generic method for the investigation of interphases in the nanocomposites.

Turning to the out-of-plane wave propagation, the BLS spectra of PDMS-filled AAO [Fig. 2(d)] display a single doublet (3) irrespective of the porosity, but for comparable wave vectors it appears at much lower frequencies than the doublet (1) belonging to the in-plane phonon propagation [Fig. 2(c)]. Moreover, doublet (3) is absent in air-filled AAO. Based on the dispersion $\omega(q)$ displayed in Fig. 3 (light gray area), branch (3) is acoustic with a phase velocity (980 m/s) being slightly slower than in PDMS and in very good agreement with the computed value of this branch [Fig. 1(b)]. This channel for phonon propagation through the materials located in the nanopores becomes inactive in air-filled AAO. As indicated by the displacement map [mode C in Fig. 1(c)], this mode is confined to the PDMS, whereas it penetrates only slightly into the AAO scaffold. Hence its phase velocity exceeds the value of $c_{PDMS}$ (in the PDMS cylinders) used in
the FDTD calculations. The out-of-plane dispersion includes an additional longitudinal acoustic phonon (5) appearing at much higher frequencies than branch (1) for the in-plane phonon propagation (Fig. 3); only branch (5) is active in air-filled AAO. This strikingly different out-of-plane phonon propagation (Fig. 3) is predicted in the theoretical band diagrams [Figs. 1(a) and 1(b)] and rationalized in the elastic displacement field distributions seen in Fig. 1(c). For example, the sound velocity in AAO with \( a = 100 \) nm and \( p = 32\% \) considered as an effective medium increases from 4520 m/s (1) for in-plane propagation to 6930 m/s (5) for out-of-plane propagation (modes 1 and 5 in Fig. 3). We recall that for the longitudinal branch (5) the modes travel primarily through the AAO scaffold, in contrast to its counterpart (1), as revealed by the displacement field distributions [\( A'' \) versus \( A \) in Fig. 1(c)].

We have applied high-resolution BLS on AAO-based nanocomposites containing hexagonal arrays of cylindrical nanotubes filled with a liquid to demonstrate directional flow of elastic energy parallel and perpendicular to the pore axes and phonon localization. The sensitivity of gigahertz phononics to interphases may pave the way for probing interfacial interactions in hybrid systems for which conventional techniques cannot be applied. Mode confinement to the material located in the nanotubes should moreover allow monitoring a broad range of phase transitions such as crystallization and melting, mesophase formation, wetting or prewetting transitions.

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23 See EPAPS Document No. E-JCPA6-130-019912 for membrane fabrication, theoretical and experimental band structures for AAO with 11% and 65% porosity, and effective medium sound velocity. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.