Sound and noisy light: Optical control of phonons in photoswitchable structures

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We present a means of controlling phonons via optical tuning. Taking as a model an array of photosensitive materials (photoswitches) embedded in a matrix, we numerically analyze the vibrational response of an array of bistable harmonic oscillators with stochastic spring constants. Changing the intensity of light incident on the lattice directly controls the composition of the lattice and therefore the speed of sound. Furthermore, modulation of the phonon band structure at high frequencies results in a strong confinement of phonons. The applications of this regime for phonon waveguides, vibrational energy storage, and phononic transistors is examined.

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Light-matter interactions are of great utility for many of applications. For mechanical vibrations (phonons) these applications encompass creating or destroying phonons using light (optomechanics \cite{1,2}, Raman scattering \cite{3–7}), creating or destroying light using phonons (vibrionic spectroscopy \cite{8}, blackbody radiation \cite{4}), and shifting the refractive index using phonons (acousto-optics \cite{9–11}). However, the last quadrant of this interaction (Table I), the control of phonon properties (e.g., speed of sound $c_s$) using light remains unexplored. As a result, acousto-optic devices (filters, modulators) are common, whereas controlling phonons remains difficult. Fundamentally, phononic devices require more than the manipulation of phonon populations, but also the tunable manipulation of speed and transmission (phase and amplitude) \cite{12–14}. Optical control, a fast, noncontact technique, is a natural candidate for this. The absence of existing optical control methods for phonons is surprising, as it is well known both that light can tune other material properties (particularly magnetic and electronic properties) by means of inducing structural phase transitions (also known as nonlinear phonics, ionic Raman) \cite{5–7,15–19}, and that other signals (pressure, temperature) can control $c_s$ and phonon dispersion (often by phase transitions) \cite{12–14,20–29}. As far as we are aware, the only research that came close to the problem of optical control were Refs. \cite{30–32}. Reference \cite{30} showed that the vibrational properties of a material can be optically switched in photosensitive liquid crystal polymers, but the optical excitation was intense enough for complete switching, so their focus was to responsive liquid crystal polymers, but the optical excitation properties of a material can be optically switched in photonic materials (photoswitches) embedded in a matrix, we numerically analyze the vibrational response of an array of one-dimensional (1D) simple harmonic oscillators (SHOs) without further loss of generality.

We therefore model a system of $n$ masses ($m \equiv 1$) joined to $N = n + 1$ photoswitchable SHOs (ground state spring constant $k_D$, excited $k_E$) with a mechanical driving force $F = F_0 \cos(\omega_0 t)$ at frequency $\omega_0$. Driving pumps a constant supply of energy into the system, so it is helpful to modify the standard clamped boundary conditions ($u_0 = 0 = u_n$, $u$ is displacement) by sandwiching this system between impedance matched systems of $n$ damped (damping rate $\gamma_i \equiv 1$) SHOs ($k = k_D$) and clamping these ends (see Fig. 1). In the more general case, exciting any SHO will not produce switching elsewhere (i.e., no cascades). This is plausible for sufficiently separated photosomerizing molecules and composite or multi-layered structures where only some portion is photosensitive (see the bottom of Fig. 1). However, if there are no photoswitching cascades, then the order and timing of (de)excitation greatly influence the dynamics. To avoid a biased order, switching
is randomized with Poisson statistics (excitation rate $R_D = B_D/D$ and deexcitation $R_U = A_{spont} + B_U/H$, where $H$ is photon fluence at a point and $A$ and $B$ are the Einstein coefficients [4]). This is plausible in the case of sufficiently low intensity photoexcitation that shot noise dominates (i.e., individual photon trajectories are relevant, not an ensemble of photons) but is also a technique for ensuring the robustness of the response to changes in the switching order. Switching dynamics is typically complicated, but because the photoexcitation is much faster than any structural rearrangement, these complexities can be neglected (to lowest order) by integrating out the shorter time scales to give

$$\dot{u}(t) = -\gamma_k(k(t) - k_{SS}(w)),$$

where $\gamma_k$ determines the rate of the structural reaction [typically $O(\omega_0)$], $k_{SS}$ is the new steady state, and $w$ denotes the stochastic variable describing switching. In principle, a change in the equilibrium position of the lattice is also possible. But our system models a photoswitch embedded in a matrix and does not describe the (realization-dependent) dynamics of modes shorter than one supercell, so this shift is negligible. Hence, the displacement obeys

$$\ddot{u}_i(t) = k_i(t)[u_{i-1}(t) - u_i(t)] + k_{i+1}(t)[u_{i+1}(t) - u_i(t)],$$

where $i$ indexes the site.

At steady state this system’s eigenmode distribution is solvable using random matrix theory (RMT) [36]. However, this does not describe the effects of changing composition (i.e., traversing the RMT’s solution space [37]). Moreover, the eigenfunctions for a single equation can be solved—exponential wave functions when no switching is occurring and modified Bessel functions of imaginary order when switching is occurring—but the inconsistency of this basis set impedes an analytic solution for any nontrivial realization. As such, we integrate the solutions numerically. Switching times/locations, being stochastic, are computed using the Gillespie algorithm [38], and the system can be integrated analytically between switchings. The initial conditions are $u(x,0) = \bar{u}(x,0)$ and $k_i(0) = k_D$. We use natural units: $a$ is the equilibrium site separation for length and $t_\gamma = 1/\gamma_a$ for time. Using $k_D = 1/t_\gamma^2$, $k_U = 2/t_\gamma^2$, $R_U = 1.5/t_\gamma$, $R_D = 2/t_\gamma$, $F_0 = 1a/t_\gamma^2$, a sample of size $n = 29$ is calculated for interval $T = 100t_\gamma$, giving $u(x,t)$ and $k(x,t)$ at various $\omega_0$.

Given the connection between $u(x,t)$ and $k(x,t)$, plotting them together is useful. Hence we present an unusual visualization scheme in Fig. 2 (alternatively, see the movies in the Supplemental Material [39]). The $x$ axis denotes the position along the chain (0 to $N$), $y$ time, colored isoval curves are the oscillator amplitude $u$, and the rectangles are the lattice composition $k$ (gray = ground state, white = excited). For clarity, Fig. 2(a) is supplemented with two subplots. The bottom subplot shows $u(i,t)$ and $k(i \pm 1,t)$ for fixed position $i$. The side subplot shows $u(x,t_0)$ and $k(x,t_0)$ for fixed time $t_0$. This is early in our simulation, so the driving signal (from $x = 0$) has not yet propagated along the lattice. Since at low frequencies [Fig. 2(a)] we expect wavelengths $\lambda \gg a$, thus the effect of the switching is a weak perturbation that distorts $u$. For shorter wavelengths [Fig. 2(b)], the solutions are more sensitive to lattice composition and may be scattered at the composition boundaries (reflecting incident phonons). However, because the lattice composition changes, transmission and reflection fluctuate, giving intervals of strong transmission or reflection. This constitutes a potential mechanism for ultrafast control of thermal conductivity. For even higher frequencies [Fig. 2(c)] the system is above the band edge of one state but not the other [i.e., above $\omega_{\min}(k_{max}) = \omega_{\min}/2/t_\gamma$. This implies that oscillations decay in one state but freely propagate in the other, allowing tunneling. In this case changing composition allows standing waves to be trapped and so could potentially store or steer vibrations. This could also be a form of phononic memory or (detailed later) a phononic transistor. Finally, at frequencies above the band edge of both configurations ($\omega > 2\sqrt{2}/t_\gamma$, not shown), no propagation is possible and the solution decays.

Analyzing $u(x,t;\omega)$ shows that photoswitching dramatically affects the transmission and dynamics, but this frequency dependence is also useful for finding the dispersion and thereby $c_\gamma$. To generate the dispersion, we Fourier transform $u(x,t)$, giving $u(q,\omega)$. The location of the maxima of $u(q,\omega)$ indicates the mode $\omega(q)$ that was excited by driving at $\omega_0$. (To generate a smooth dispersion rather than a series of discrete normal modes, $n = 124$ is used.) This is repeated for $N_{rep} = 10$ times with $T = 200t_\gamma$ for ergodicity, and $\omega$ and $q$ are averaged. Because at high frequencies the waves can be narrowly confined, this will artificially introduce Fourier components near the $\Gamma$ point. Since these are not features of

\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
Photon $\rightarrow$ phonon & Optomechanics, Raman \\
\hline
Phonon $\rightarrow$ photon & Vibronics, fluorescence, Acousto-optics \\
\hline
\end{tabular}
\caption{The quadrants of light-matter interaction. The first row is light used to control phonons, and the second is sound used to control photons. The first column is changing populations, and the second is changing dispersion.}
\end{table}
The steady state compositions are
\[ \frac{N_U}{N} = \frac{R_D}{R_D + R_U} = \frac{(g_U/g_D)H}{S(\omega_\nu) + (1 + g_U/g_D)H} \]  
(5)
where \( g_{U,D} \) are the mode degeneracies, \( S = 2\hbar \omega_\nu^3/\pi c^3 \), and \( \omega_\nu \) is the photon frequency (the last relation comes from a detailed balance of the Einstein coefficients [4]). Changing \( R_U/R_D \) changes \( N_U/N_D \), so increasing the optical intensity increases the equilibrium population in the excited state (to some limiting fraction given by the mode degeneracies). Therefore,
changing illumination gives direct control of $c_1$. Now, consider a simple kinetic model where $c_1$ in the ground (excited) state is $c_{1,D}$ ($c_{1,U}$). The average speed for an inhomogeneous system would be the weighted average $c_{1,D} N_D / N + c_{1,U} N_U / N$ or $c_{1}(\text{kin}) = c_{1,D} + (c_{1,U} - c_{1,D}) N_U / N$, \( i.e., \) linear with composition. This disagrees with our observed relation, which falls below this kinetic limit except for the homogeneous cases of $N_U / N = 0$ or 1, which agree with the analytic results to within 99% accuracy (see Fig. 3 inset). This is expected, though, as reflections delay a pulse and decrease its effective velocity.

Finally, consider again the confined regime. In the homogeneous cases the transmittivity of the material should be nearly 1 \( i.e., \) no loss \( o r \) 0 \( i.e., \) perfect damping) for a sufficiently thick sample. Switching between these compositions (possible when $g_U \gg g_D$ and the photon intensity is large, or stochastically possibly for $R_D > R_U$ and $N \approx g_U / g_D$) allows for illumination controlled switching between transmission and reflection. Dynamically changing $R_D / R_U$ therefore allows for controlled phonon transmission. This switching mechanism is therefore a potential phononic transistor using the optical analog indirect control scheme presented in Ref. [14] \( i.e., \) a light source instead replaces the electromagnet). Such an indirect transistor is more easily tuned than the direct designs, which rely upon phonon-phonon couplings [29] that are not dynamically accessible. To show the feasibility of this proposal, we repeat our calculations for a pulsed illumination $\{R_D^{\text{on}} = 4 / \tau_p, R_D^{\text{off}} = 0\}$. Pulse widths are selected such that a homogeneous composition is produced for each state. Since complete, monotonic switching of a sample has the expectation value $R_{U,D} c_{U,D}(N) = N \sum_{l=1}^{N} 1^l = N H_N \approx N \ln N$, \( 7 \)

where $H_N$ is the harmonic function, we use a sample size of $n = 9$ for these simulations (illumination period $200 \tau_p$, dark period $200 \tau_p$, total run time $2000 \tau_p$, $R_D = 4 / \tau_p = 8 R_U$). Plotting the amplitude at the far end of the sample (normalized to the maximum amplitude without damping $\max[u(L,t)]$) gives Fig. 4 for a $\omega = 2.1 / \tau_p$. The horizontal lines indicate the rms average amplitude during each period of darkness or illumination (including switching intervals, wherein underestimating the difference). For frequencies below $\omega_p$ there is transmission for both states, so the ratio of these averages is nearly 1 (not shown), whereas for frequencies just above $\omega_p$ there is a large difference between the states and so a large separation is observed (Fig. 4). As frequency increases above $\omega_p$, transmission drops and the ratio again approaches 1 (not shown). Comparing these results with Fig. 2(c) reveals a crossover from confinement to transmission with increasing photon intensity. For confinement to be effective, there should be narrow domains of the propagating configuration, which is best achieved with weak driving.

In summary, we have demonstrated an approach controlling the phononic properties of a system, using light to tune the phonon band structure. This reverses the acousto-optic formulation of phonons modulating the index of refraction, and instead light modulates $c_1$. The shifting of the dispersion that this allows opens several interesting possibilities for phononic devices. Delay lines and, by extension, phase control gates can be constructed by tuning the speed of sound. Thermal conductivity modulation is clearly achievable by the controlled scattering of short-wavelength phonons from the configuration boundaries. Vibrational energy storage or phononic memory are possible in the high frequency regime with phonon confinement under weak optical driving, and under the same regime with strong optical driving, an optophononic switch or indirect phononic transistor is feasible. The control of the speed of sound could also improve the short-term storage (RAM) of phononic information through delay line memory, similar to Ref. [40]. Furthermore, the patterning of photoswitches in a system—or their patterned photoexcitation—allows for real-time, adaptable phononic materials, including phononic crystals and metamaterials. This can be particularly useful (in the confinement regime) for creating waveguides that dynamically control the propagation of phonons or for tuning the thermal conductivity by selectively introducing scatterers. Such an approach would also be experimentally feasible, as an optically controlled bandpass filter was proposed using a superlattice of resonant cavities with chalcogenide glasses in [41] (only light or dark states were simulated and so no intensity-dependent tunability was observed). Similar approaches for experimentally realizing these devices could be achieved by superlattices of photosensitive materials (e.g., photoisomers [30], ionic Raman-active materials [31], photoelastic glasses such as chalcogenides [32]) separated by inactive layers or by embedding these photosensitive materials (particularly photoisomers, which are generally small organic molecules) within an inactive matrix (the scenario illustrated in Fig. 1). Finally, the prevalence of phonon couplings in quantum computing, electronics, phoxonics, and spintronics [42–46] implies that these effects may have further applications in the optical control of a great many signals in a cavalcade of fields.

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[35] Thermalization and velocity modulation are distinct effects, assuming sufficiently weak nonlinearity to the lattice. Considering a current of phonons $J = n v$, thermalization will change the number of phonons $n$ while structural changes will change the velocity $v$. It is only when anharmonicity is so strong that this distinction breaks down. Even then, the use of low amplitude phonons makes this negligible.
[37] Changing compositions is also equivalent to traversing different realizations of a glassy or disordered medium, or taking an ensemble average over disorder.