Nanophotonics with optical phonons in two dimensions

Nicholas Rivera,[1,2,*] Thomas Christensen,[2] and Prineha Narang[1,†]

[1]*John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA*
[2]*Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, USA*

(Dated: November 7, 2018)

Extreme confinement of electromagnetic energy by phonon polaritons promises extremely strong and novel forms of control over the dynamics of matter. To bring such control to its ultimate limit, it is important to consider phonon polaritons in two dimensional systems. However, recent studies have pointed out that in two-dimensional systems, splitting between longitudinal and transverse (LO and TO) optical phonons, which is necessary for the existence of phonon polaritons in three dimensions, is absent. The question then arises as to whether the ability to exploit optical phonons disappears in lower dimensions. Here, we settle this question, finding that the phonon-polariton of the bulk is essentially replaced by the LO phonon. We present the confinement and propagation losses of LO phonons. We then calculate various measures of strong light-matter interaction such as single and two-photon spontaneous emission enhancement, and discuss methods such as EELS to probe these excitations.

In this Letter, we ...

I. ELECTRODYNAMICS OF OPTICAL PHONONS IN TWO-DIMENSIONS

In this section, we develop the theory of electromagnetic waves associated with optical phonons in two dimensions. The crux of the theory isdetermining the dielectric permittivity associated with the monolayer. It is obtained by considering the response of the ions in the monolayer to a longitudinal electromagnetic wave whose electric field is the gradient of a scalar potential ϕ. The coupling Hamiltonian is then given by

$$H_{\text{int}} = \int d^2x \rho\phi = -\int d^2x (\nabla \cdot \mathbf{P})\phi, \tag{1}$$

with ρ the charge density and $\mathbf{P}$ the polarization density associated with the ionic motion. The polarization can be expanded in powers of the displacement of the ions. In particular, we can consider the polarization P_i generated in the monolayer when atom κ of the unit cell is displaced along the j direction by amount $u_{\kappa,j}$. To lowest order:

$$P_i - P_i^0 = \Omega \frac{\partial P_i}{\partial u_{\kappa,j}} u_{\kappa,j} \equiv Z_{\kappa,ij} u_j, \tag{2}$$

where $Z_{\kappa,ij}$ is the Born effective charge tensor of ion κ and Ω is the unit cell area. With this relation between polarization and ionic displacements, we have expressed the Hamiltonian as a coupling between the scalar potential and ionic displacements. We consider the response of the monolayer to a scalar potential of the form $\phi = \phi(\mathbf{q},\omega)e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}$, where $\mathbf{q}$ is a two-dimensional wavevector in the plane of the monolayer. Such a potential corresponds to a longitudinal electric field of the form $\mathbf{E} = i\mathbf{q}\phi(\mathbf{q},\omega)e^{i\mathbf{q}\cdot\mathbf{r}-i\omega t}$. It follows that the induced polarization takes the form $P_i = \epsilon_0 \Pi_{ij}(\mathbf{q},\omega) E_{j,\text{tot}}(\mathbf{q},\omega)$, where $\Pi_{ij}(\mathbf{q},\omega)$ is the polarization-polarization response function of the monolayer and $E_{j,\text{tot}}(\mathbf{q},\omega)$ is taken as the *total* field which is a sum of the applied field and the field created by induced polarization. The polarization-polarization response function is given by

$$\mathbf{\Pi}(\mathbf{q},\omega) = \frac{1}{\epsilon_0 \Omega} \sum_{m,n} \frac{\mathbf{P}_{mn}(\mathbf{q}) \otimes \mathbf{P}_{nm}(\mathbf{q})}{\hbar\omega + E_{nm} + \mathrm{i}0^+} \left(\mathrm{e}^{\beta E_m} - \mathrm{e}^{\beta E_n} \right), \tag{3}$$

where m,n are states of the phononic Fock space of the monolayer, $P_{i,mn} = \sum_{\kappa,j} \langle m|u_{\kappa,j}|n\rangle$ are matrix elements of the polarization associated with phonon modes, $E_{m(n)}$ is the energy of state m (n), and β is the inverse temperature. Evaluating the contribution of optical phonons in the harmonic approximation to the polarization-polarization response, one finds that the response function is given by:

$$\Pi_{qq}(\mathbf{q},\omega) = \frac{1}{\epsilon_0 \hbar \Omega} \frac{2\omega_{\mathbf{q}L}}{\omega_{\mathbf{q}L}^2 - \omega^2} |\hat{q} \cdot \langle 1_{\mathbf{q}L}|\mathbf{P}(\mathbf{q})|0_{\mathbf{q}\sigma}\rangle|^2, \tag{4}$$

where 'L' denotes longitudinal polarization, $|0_{\mathbf{q}L}\rangle$ ($|1_{\mathbf{q}L}\rangle$) denotes a state with no (one) longitudinal phonon of wavevector $\mathbf{q}$. The frequency $\omega_{\mathbf{q}L}$ in the denominator, as in the case of bulk phonons, is the frequency of the longitudinal phonon of wavevector $\mathbf{q}$ prior to considering LO-TO splitting [Needs reference!]. This is the consistent with the fact that LO-TO splitting is a collective effect arising from Coulomb interactions and the fact that the equation above represents a single-particle susceptibility. Coulomb interactions are accounted for in the random phase approximation, and to include them in the single-particle response would be double-counting. The component qq in the response tensor denotes a pair of directions parallel to the wavevector. To relate the polarization-polarization response function to the electromagnetic modes supported by a polar monolayer, we solve Maxwell's equations for an evanescent electromagnetic mode supported by a surface with polarization-polarization response tensor Π. We consider the monolayer to be sandwiched by a superstrate of permittivity ϵ_1 and a substrate of permittivity ϵ_2.

To strip the analysis to its bare essentials, we consider optical phonon response with in-plane isotropy in the long-

wavelength limit arising from in-plane LO oscillations. A relevant example of a system where these conditions are satisfied is in a hexagonal boron nitride monolayer, considering optical phonons in the so-called upper Reststrahlen band which in bulk spans the frequency range of 1360 to 1610 cm^{-1}. In a monolayer geometry with translation invariance and in-plane isotropy, the electromagnetic modes of Maxwell's equations can be composed into transverse magnetic (TM) and transverse electric (TE), where the magnetic or electric field respectively is transverse to the in-plane wavevector of the mode. In practice, it is the TM mode which is associated with highly confined electromagnetic waves that are of use in nanophotonics. TE waves are not supported at the same frequency as transverse magnetic waves, and require exotic conditions to be realized in two-dimensional materials. Given the isotropy, we may suppress indices from the response tensor. We may also consider without further loss of generality a TM mode with wavenumber q along the x-direction in the monolayer and magnetic field $H(z)e^{iqx-i\omega t}$ along the y-direction of the monolayer. The direction transverse to the monolayer is denoted as z. With these definitions in place, the Maxwell equation satisfied by the magnetic field is

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}z^2}+q^2-\epsilon_{\mathrm{env}}\frac{\omega^2}{c^2}\right)H(z)=0. \tag{5}$$

We consider a solution of the form $H(z)=e^{-\kappa_1 z}$ for $z>0$ with $\kappa_1=\sqrt{q^2-\epsilon_1\frac{\omega^2}{c^2}}$ and a solution of the form $H(z)=ce^{\kappa_2 z}$ for $z<0$ with $\kappa_2=\sqrt{q^2-\epsilon_2\frac{\omega^2}{c^2}}$. The boundary condition on the magnetic field is $H_y^{(+)}-H_y^{(-)}=-K_x=\mathrm{i}\omega\mathbf{P}_x$ where $\mathbf{K}$ is the surface current density, expressed through the polarization density $\mathbf{P}$ of the monolayer. This condition enforces $c=(1+\frac{\epsilon_0}{\epsilon_2}\kappa_2\Pi)^{-1}$. Continuity of the electric field in the x direction enforces $\frac{\epsilon_2}{\epsilon_1}=-\frac{\kappa_2}{\kappa_1}c$. These two conditions fully specify the TM mode. To simplify the discussion, we consider the so-called electrostatic limit, it in which the wavenumber q of the TM mode is much larger than the free-space wavenumber $\frac{\omega}{c}$. This is well-satisfied in monolayer optical phonons in 2D. With this approximation, the condition for a TM mode corresponding to an optical phonon is

$$\epsilon_{\mathrm{env}}+\frac{1}{2}\epsilon_0 q\Pi(q,\omega)\equiv\epsilon_{\mathrm{RPA}}(\omega)=0. \tag{6}$$

The quantity $\epsilon_{\mathrm{RPA}}(\omega)=0$ coincides with the phonon contribution to the longitudinal dielectric function of the monolayer in the random-phase approximation.

To proceed, we express the polarization matrix element in Equation (4) in terms of parameters of the monolayer such as the Born effective charges. Considering the longitudinal phonon contribution to the second-quantized ionic displacement, as in [Needs reference!], one finds that the RPA dielectric function is given by:

$$\epsilon_{\mathrm{RPA}}(\omega)=\epsilon_{\mathrm{env}}-\frac{q}{2\epsilon_0}\frac{\left|\hat{q}\cdot\sum_{\kappa,j}Z_{\kappa,ij}\eta_{\kappa,j}\right|^2}{\omega_{\mathrm{TO}}^2-\omega^2} \tag{7}$$

In this expression, ω_L and been re-named as ω_{TO}, because in the absence of LO-TO splitting, they are degenerate. Additionally, we have defined eigendisplacements $\boldsymbol{\eta}_{\kappa\mathbf{q}}\equiv\frac{e_{\kappa\mathbf{q},L}}{\sqrt{M_\kappa}}$, where $e_{\kappa\mathbf{q},L}$ is the unit-normalized polarization vector of atom κ in the unit cell oscillating according to a longitudinal phonon of wavevector $\mathbf{q}$ and M_κ is the mass of atom κ.

As is well known, the zeros of the RPA dielectric function, denoted $\omega_{\mathbf{q}}$, correspond to longitudinal electromagnetic waves. Thus, the condition for the zeros of the dielectric function correspond to

$$\begin{aligned}\omega_{\mathbf{q}}^2-\omega_{\mathbf{q},\mathrm{TO}}^2&=\frac{e^2}{2\epsilon_0\epsilon_{\mathrm{env}}q}\frac{1}{\Omega}q^2\Big|\sum_{\kappa,j}Z_{\kappa,ij}\eta_{\kappa,j}\Big|^2\\&=V(q)\frac{1}{\Omega}q^2\Big|\sum_{\kappa,j}Z_{\kappa,ij}\eta_{\kappa,j}\Big|^2,\end{aligned} \tag{8}$$

where $V(q)$ is the Coulomb interaction in two dimensions, screened by the dielectric environment of the sub- and superstrates. This result, as we now show, reveals that the TM mode corresponds simply to the two-dimensional optical phonon. In particular, it was shown in [Sohier2017] that in two-dimensional polar materials, the extra restoring forces on LO phonons relative to TO phonons, due to the Coulomb interaction, lead to a wavevector-dependent LO-TO splitting given by Equation (8) of the current manuscript. *Thus, one of the main results of our manuscript is that the wave solutions Maxwell's equations associated with phonon-polaritons in bulk materials, correspond to pure LO phonons in the monolayer limit.*

We now re-write ϵ_{RPA} in a way that is expressed purely in terms of the optical phonon dispersion, derive the conductivity of the monolayer, and derive a universal form for the dispersion of 2D LO phonons in the long-wavelength limit. From Equation (8), we may write Equation (7) as

$$\epsilon_{\mathrm{RPA}}(\omega)=\epsilon_{\mathrm{env}}\left(1+\frac{\omega_{\mathbf{q}\mathrm{LO}}^2-\omega_{\mathbf{q}\mathrm{TO}}^2}{\omega_{\mathbf{q}\mathrm{TO}}^2-\omega^2}\right). \tag{9}$$

Similarly, the conductivity is prescribed by $\sigma(\mathbf{q},\omega)=-\mathrm{i}\omega\Pi(\mathbf{q},\omega)$. We are now in a position to derive a universal form for the RPA dielectric function of a 2D polar slab in terms of three phenomenological parameters. In many cases [ref], the Born charges are independent of q for small q, and thus the dispersion can be written as

$$\omega_{\mathbf{q},LO}=\sqrt{\omega_{\Gamma\mathrm{TO}}^2+\mathcal{S}q}\approx\omega_{\Gamma\mathrm{TO}}+v_g q, \tag{10}$$

where $\mathcal{S}$ is a microscopic constant determined by the Born charges of the monolayer, v_g is the group velocity of the LO

mode, and $\omega_{\Gamma\mathrm{TO}}$ is the TO phonon frequency at the Γ point. Then, the universal form of the dispersion relation

$$\epsilon_{\mathrm{RPA}}(\omega) = \epsilon_{\mathrm{env}}\left(1 + \frac{2v_g\omega_{\mathbf{q}\mathrm{TO}}}{\omega_{\mathbf{q}\mathrm{TO}}^2 - \omega^2 + \mathrm{i}\omega\tau^{-1}}\right). \tag{11}$$

where we have also phenomenologically included the phonon dissipation rate τ^{-1}, consistently with a relaxation-time prescription. Thus, all of the optical properties associated with LO phonons is captured by the TO phonon frequency, the slope of the LO dispersion at Γ, and the dissipation τ^{-1}.

II. STRONG LIGHT-MATTER INTERACTIONS ENABLED BY 2D OPTICAL PHONONS

We now move to analyze key figures of merit of 2D LO phonons.

A. Spontaneous emission

B. Spontaneous and stimulated electron energy loss

III. ACKNOWLEDGEMENTS

N. R. recognizes the support of the DOE Computational Science Graduate Fellowship (CSGF) fellowship no. DE-FG02-97ER25308. P. N. acknowledges start-up funding from the Harvard John A. Paulson School of Engineering and Applied Sciences. T. C. acknowledges support from the Danish Council for Independent Research (Grant No. DFF–6108-00667). The authors thank Joshua Caldwell (Vanderbilt), Dmitri Basov (Columbia), Ido Kaminer (Technion), Siyuan Dai (UT Austin), and Samuel Moore (Columbia) for helpful discussions. This work was supported by the DOE Photonics at Thermodynamic Limits Energy Frontier Research Center under grant no. DE-SC0019140.

* nrivera@seas.harvard.edu
† prineha@seas.harvard.edu

1 J. D. Caldwell *et al.*, Nano Lett. **13**, 3690 (2013).
2 X. G. Xu, J.-H. Jiang, L. Gilburd, R. G. Rensing, K. S. Burch, C. Zhi, Y. Bando, D. Golberg, and G. C. Walker, ACS Nano **8**, 11305 (2014).
3 J. D. Caldwell *et al.*, Nat. Commun. **5**, 5221 (2014).
4 S. Dai *et al.*, Science **343**, 1125 (2014).
5 A. Tomadin, A. Principi, J. C. Song, L. S. Levitov, and M. Polini, Phys. Rev. Lett. **115**, 087401 (2015).
6 E. Yoxall, M. Schnell, A. Y. Nikitin, O. Txoperena, A. Woessner, M. B. Lundeberg, F. Casanova, L. E. Hueso, F. H. Koppens, and R. Hillenbrand, Nat. Photonics **9**, 674 (2015).
7 P. Li, M. Lewin, A. V. Kretinin, J. D. Caldwell, K. S. Novoselov, T. Taniguchi, K. Watanabe, F. Gaussmann, and T. Taubner, Nat. Commun. **6**, 7507 (2015).
8 S. Dai *et al.*, Nat. Commun. **6**, 6963 (2015).
9 S. Dai *et al.*, Nat. Nanotechnol. **10**, 682 (2015).
10 J. D. Caldwell, L. Lindsay, V. Giannini, I. Vurgaftman, T. L. Reinecke, S. A. Maier, and O. J. Glembocki, Nanophotonics **4**, 44 (2015).
11 P. Li, X. Yang, T. W. Maß, J. Hanss, M. Lewin, A.-K. U. Michel, M. Wuttig, and T. Taubner, Nat. Mater. **15**, 870 (2016).
12 D. N. Basov, M. M. Fogler, and F. J. García de Abajo, Science **354**, aag1992 (2016).
13 D. Basov, R. Averitt, and D. Hsieh, Nat. Mater. **16**, 1077 (2017).
14 T. Low, A. Chaves, J. D. Caldwell, A. Kumar, N. X. Fang, P. Avouris, T. F. Heinz, F. Guinea, L. Martin-Moreno, and F. Koppens, Nat. Mater. **16**, 182 (2017).
15 A. J. Giles *et al.*, arXiv:1705.05971 (2017).
16 R. Hillenbrand, T. Taubner, and F. Keilmann, Nature **418**, 159 (2002).
17 A. Kumar, T. Low, K. H. Fung, P. Avouris, and N. X. Fang, Nano Lett. **15**, 3172 (2015).
18 N. Rivera, G. Rosolen, J. D. Joannopoulos, I. Kaminer, and M. Soljačić, Proc. Natl. Acad. Sci. U. S. A. **(ahead of print)**, 201713538 (2017).
19 Y. Kurman, N. Rivera, T. Christensen, S. Tsesses, M. Orenstein, M. Soljačić, J. D. Joannopoulos, and I. Kaminer, Nat. Photonics **12**, 423 (2018).
20 M. Jablan, H. Buljan, and M. Soljačić, Phys. Rev. B **80**, 245435 (2009).
21 F. Stern, Phys. Rev. Lett. **18**, 546 (1967).
22 T. Sohier, M. Gibertini, M. Calandra, F. Mauri, and N. Marzari, Nano Lett. **17**, 3758 (2017).
23 R. V. Gorbachev *et al.*, Small **7**, 465 (2011).
24 T. T. Tran, K. Bray, M. J. Ford, M. Toth, and I. Aharonovich, Nat. Nanotechnol. **11**, 37 (2016).
25 M. Jablan, M. Soljačić, and H. Buljan, Proc. IEEE **101**, 1689 (2013).
26 A. Manjavacas, F. Marchesin, S. Thongrattanasiri, P. Koval, P. Nordlander, D. SÃąnchez-Portal, and F. J. GarcÃŋa de Abajo, ACS Nano **7**, 3635 (2013).
27 A. Lauchner, A. E. Schlather, A. Manjavacas, Y. Cui, M. J. McClain, G. J. Stec, F. J. GarcÃŋa de Abajo, P. Nordlander, and N. J. Halas, Nano Lett. **15**, 6208 (2015).