

Nanophotonics with optical phonons in two dimensions

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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. Recent studies have pointed out that in two-dimensional systems, splitting between longitudinal and transverse (LO and TO) optical phonons is absent at the Γ point. Does this lack of LO-TO splitting imply the lack of a strongly confined electromagnetic (phonon-polariton) mode in polar monolayers? Here, we derive a universal form for the spatially-nonlocal dielectric function of a polar monolayer specified by: the TO phonon frequency, the non-zero group velocity of the LO phonon, and the phonon lifetime. Our analysis reveals that the phonon-polariton of the bulk is “replaced” by the LO phonon. We present the confinement and propagation losses of LO phonons, finding that high LO phonon confinement and reasonable propagation quality factors coincide in regions which are difficult to detect with near-field optical microscopy, but may be more amenable to electron energy-loss spectroscopy. Finally, we show that 2D LO phonons in hBN present extremely strong light-matter interactions with external emitters, providing possibilities for 10,000,000-fold enhanced spontaneous emission and strong coupling with vibrational emitters.

Phonon polaritons, hybrid quasiparticles of photons and optical phonons supported in polar materials, offer great promise for deeply sub-diffractive control of electromagnetic fields at mid-IR and THz frequencies. Phonon polaritons share many features in common with plasmon polaritons in conductors. In recent years, it has been shown that phonon-polaritons enable confinement of light to volumes over 10^6 times smaller than that of a diffraction-limited photon in free-space.^{1–15} Due to this remarkable confinement and their relatively high lifetimes of around picoseconds, phonon-polaritons open new opportunities for vibrational spectroscopy, radiative heat transfer,¹⁶ and control of dynamics in quantum emitters.^{17–19} In many cases, extreme confinement of phonon polaritons is achieved by the use of thin-films, which shrink the in-plane and out-of-plane wavelength of polaritons monotonically with decreasing film thickness. In many cases, a monolayer is the ultimate limit of this effect. Thus, to bring these classical and quantum nanophotonics applications to their ultimate limits, it is necessary to consider the properties of these modes in two-dimensions. However, this picture of monolayers supporting maximally confined phonon-polariton modes is ostensibly complicated by the fact that in two-dimensional polar materials, the LO-TO splitting that gives rise to phonon-polaritons in three-dimensions is absent at the Γ point.

In this Letter, we develop core results in the nascent field of optical phononics in two-dimensional materials by deriving a universal form for the dielectric function of a polar monolayer, incorporating spatially nonlocal effects, which is specified in fully in terms of the dispersion relation of LO and TO phonons in two dimensions. Using these parameters for important monolayers such as hexagonal boron nitride, we present the confinement and propagation losses of these modes, identifying the frequency region where they should be most easily detected. We then show that these modes es-

entially provide the ultimate limit of light-matter interaction between emitters and polar materials, showing that for atom-like emitters, their spontaneous decay can be enhanced seven orders of magnitude by the emitter-LO phonon coupling. For free-electrons, we show a substantial probability of multiple LO phonon excitation can occur.

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 is determining 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

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

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:

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

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

$$\Pi(\mathbf{q}, \omega) = \frac{1}{\epsilon_0 \Omega} \sum_{m,n} \frac{\mathbf{P}_{mn}(\mathbf{q}) \otimes \mathbf{P}_{nm}(\mathbf{q})}{\hbar\omega + E_{nm} + i0^+} (e^{\beta E_m} - e^{\beta E_n}), \quad (3)$$

where m, n are states of the phononic Fock space of the monolayer, $P_{i, mn} = \sum_{\kappa, j} Z_{\kappa, ij} \langle m | u_{\kappa, j} | n \rangle$ 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:

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

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 is an uncontrolled 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

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

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 $H_y^{(+)} - H_y^{(-)} = -K_x = i\omega \mathbf{P}_x$ 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

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

The quantity $\epsilon_{\text{RPA}}(\omega) = 0$ 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:

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

In this expression, ω_L has been re-named as ω_{TO} , because in the absence of LO-TO splitting, they are degenerate. Additionally, we have defined eigendisplacements $\eta_{\kappa\mathbf{q}} \equiv \frac{e\kappa\mathbf{q} \cdot \mathbf{L}}{\sqrt{M_\kappa}}$,

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 can be expressed as

$$\begin{aligned}\omega_{\mathbf{q}}^2 - \omega_{\mathbf{q},\text{TO}}^2 &= \frac{e^2}{2\epsilon_0\epsilon_{\text{env}}q} \frac{1}{\Omega} q^2 \left| \sum_{\kappa,j} Z_{\kappa,j}^r \eta_{\kappa,j} \right|^2 \\ &= V(q) \frac{1}{\Omega} q^2 \left| \sum_{\kappa,j} Z_{\kappa,j}^r \eta_{\kappa,j} \right|^2,\end{aligned}\quad (8)$$

where $eZ^r = Z$, with e the electron charge, and $V(q)$ 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

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

Similarly, the conductivity is prescribed by $\sigma(\mathbf{q},\omega) = -i\omega\Pi(\mathbf{q},\omega)$. 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

$$\omega_{\mathbf{q},\text{LO}} = \sqrt{\omega_{\Gamma\text{TO}}^2 + S}q \approx \omega_{\Gamma\text{TO}} + v_g q, \quad (10)$$

where S is a microscopic constant determined by the Born charges of the monolayer, v_g is the group velocity of the LO mode, and $\omega_{\Gamma\text{TO}}$ is the TO phonon frequency at the Γ point. The group velocity is specified in terms of microscopic parameters via

$$v_g = \frac{e^2}{4\epsilon_0\epsilon_{\text{env}}\omega_{\Gamma\text{TO}}\Omega} \left| \sum_{\kappa,j} Z_{\kappa,j}^r \eta_{\kappa,j} \right|^2. \quad (11)$$

Thus, in the long wavelength limit, we have the following universal parameterization of the RPA dielectric function of

a polar monolayer:

$$\epsilon_{\text{RPA}}(\omega) = \epsilon_{\text{env}} \left(1 + \frac{2v_g\omega_{\mathbf{q},\text{TO}}}{\omega_{\mathbf{q},\text{TO}}^2 - \omega^2 + i\omega\tau^{-1}} \right), \quad (12)$$

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} . In Table 1, we tabulate these parameters for a few polar monolayers whose phonon band-structures have been calculated in the literature: hBN, MoS₂, and ...

It has been well-appreciated in the literature on phonon polaritons in thin slabs. Here, we expand on the analogy in the two-dimensional case. To do so, we take Equation (8) in the case of a two-atom unit cell (such as hBN), and note that the term in the sum over Born charges can be written as $e^2 \left| \sum_{\kappa,j} Z_{\kappa,j}^r \eta_{\kappa,j} \right|^2 \equiv \left(\frac{eZ^r}{\sqrt{M_*}} \right)^2 \equiv \left(\frac{Q_*}{\sqrt{M_*}} \right)^2$. Then, the LO-TO

splitting can be written as $\omega_{\mathbf{q}}^2 - \omega_{\mathbf{q},\text{TO}}^2 = \frac{Q_*^2}{2\epsilon_0\epsilon_{\text{env}}M_*} q$. Now we note that the RHS is exactly the squared-frequency $\omega_{\mathbf{q},p}^2$ for a plasma oscillation in a 2D gas of charged particles with charge Q_* and mass M_* . This squared frequency can be thought of as the "LP-TP" splitting between longitudinal and transverse plasma oscillations. Of course, there are no transverse plasma oscillations, and so " $\omega_{\text{TP}} = 0$ ". In the three-dimensional plasmon case, " $\omega_{\text{TP}} = 0$ ", but the difference between the squared longitudinal and transverse plasma oscillation frequencies at zero-wavevector is non-zero and given by ω_p^2 . This analogy between phononic and plasmonic behavior as a function of dimension is illustrated schematically in Figure 1.

II. PROPERTIES OF 2D LO PHONON MODES IN MONOLAYER HBN

In Fig. 2a, we present the dispersion relation, operationally defined through the poles of the Fresnel reflection coefficient for p -polarized waves, which for a monolayer of conductivity $\sigma(\mathbf{q},\omega) = -\frac{2i\omega}{\epsilon q} (\epsilon_{\text{RPA}} - \epsilon_{\text{env}})$ below vacuum and on top of a substrate of permittivity ϵ_s , is given by

$$r_p(\mathbf{q},\omega) = \frac{(\epsilon_s - 1) - \frac{\sigma(\mathbf{q},\omega)q}{\omega\epsilon_0}}{(\epsilon_s + 1) - \frac{\sigma(\mathbf{q},\omega)q}{\omega\epsilon_0}}. \quad (13)$$

In Figs. 2b, we show the confinement factor (or effective mode index) of the 2D LO phonon mode, defined by $n_{\text{eff}} = \frac{qc}{\omega}$. The confinement factor is a key figure of merit in many nanophotonic applications involving quantum emitters, because as was shown in [Rivera], all interactions involving emission of electromagnetic energy by emitters, such as electric and magnetic dipole emission, multipole emission, phosphorescence, and multiphoton emission, scale as some power

of this confinement factor. Interestingly, in the case of a monolayer, the confinement grows very rapidly in frequency, due to the extremely low group velocity of 2D LO phonons, which is a remarkable four orders of magnitude slower than the speed of light. In particular, at frequencies of 1450 cm^{-1} , the LO phonon already has a confinement factor in excess of conf, corresponding to a phonon wavelength of $6896.55/\text{conf}$ nm, which is much shorter wavelength than any phonon polariton thus measured so far, as well as shorter wavelength than any plasmon that has been measured in the mid-IR, such as in graphene. In fact, this short wavelength is mostly out of the range of measurability in scattering near-field microscope (SNOM) measurements, which with current tip radii, are limited to measuring wavelengths in excess of 60 nm. This 2D LO phonon can be measured with SNOM at frequencies close to the TO phonon frequency, where the confinement is less, but this comes at the price of very high dissipation and correspondingly low propagation quality factor, as illustrated in Fig. 2c. This is simply because frequencies near the TO phonon, which is strongly absorbing, correspond to the highest dissipation (measured by $\text{Re } \sigma$ or $\text{Im } \epsilon_{\text{RPA}}$). These considerations imply that access to the lower-loss and higher-confined portions of the phononic waves, in the absence of a sharp tip, requires either a free electron probe, as in EELS, or a quantum emitter probe, such as a molecule or quantum well [cite people].

In what remains of this section, we discuss briefly “anomalies”, by which we mean features of the 2D LO phonon dispersion that cannot be predicted by considering the electromagnetic modes of a very thin slab of material whose dielectric function is that of the bulk polar material (with finite LO-TO splitting). For example, the long-wavelength linear dispersion of the 2D LO phonon mode given by Equation (10) is not an anomaly, as this would be predicted by taking a sub-nm thick slab of a polar dielectric material. However, the precise slope cannot be predicted, as it would depend on the thickness used for the slab, which is ill-defined, as one will find that it does not correspond to the thickness of the boron or nitrogen atoms. One immediate anomaly is that in the monolayer, there is only one LO phonon, and thus only one branch of TM modes. This is contrary to a thin slab of hexagonal boron nitride, which is hyperbolic $\epsilon_{zz} > 0, \epsilon_{xx} = \epsilon_{yy} < 0$, and thus has many branches of TM modes spaced in wavevector by an amount proportional to d^{-1} , with d the film thickness. Such additional TM modes would be incorrectly predicted by extrapolating the bulk to a film. Another anomaly comes from the fact that the dispersion relation of the 2D LO phonon is non-monotonic, and the frequency starts to decrease for sufficiently large wavevector. This can never happen by extrapolating to a monolayer a dielectric function which has finite LO-TO splitting.

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

The extreme confinement of electromagnetic fields offered by the 2D LO phonon presents an opportunity for quantum optical applications in which one seeks to couple an external emitter such as an atom, molecule, defect, or artificial atomic system to electromagnetic fields. Applications of these couplings can be to realize ultra-bright single- or two-photon sources, or realize strong-coupling and the associated phenomenology of Rabi oscillations and polaritons, or resolve spectroscopically “forbidden” transitions. In Figure 3, we show key figures of emitter-phonon coupling in polar monolayers.

In Fig. 3a, we show the enhancement (or Purcell factor) F_p of spontaneous emission of 2D LO phonons at frequency ω_0 by an external emitter at different distances d away from the surface. The rate of spontaneous emission Γ into 2D LO phonons obeys

$$\Gamma = \frac{3c^3}{2\omega_0^3} \int dq q^2 e^{-2qz} \text{Im } r_p(q, \omega_0) \times \Gamma_0 \equiv F_p(\omega_0) \Gamma_0, \quad (14)$$

where Γ_0 is the free-space spontaneous emission rate. As can be seen from Fig. 3a, for an emitter position 5 nm away from the surface, the Purcell factor can be very high, corresponding to over a million-fold increase in the rate of 2D LO phonon emission compared to photon emission into free-space. While this rate-enhancement is already quite high, it is a natural question what the highest possible spontaneous-emission rate enhancement is as a function of frequency. Recently, material-geometry-independent limits for spontaneous emission enhancement have been derived. In particular, the maximum rate of spontaneous emission enhancement is bounded by

$$\dots \quad (15)$$

This is plotted in Fig. 3b for the case of monolayer hBN.

Finally, we address one manner of externally probing 2D LO phonons without the need for SNOM or emitters: with electron energy losses in free electrons. As the energy losses under consideration will be on the order of 200 meV for single phonon excitation in monolayer hBN, the electron energy spread which determines the width of EELS peak (including the zero-loss peak) must be substantially smaller than 200 meV. Fortunately, this is possible in high-resolution EELS, which is particularly useful for probing surface phenomena, and has been applied to measure the dispersion relation of plasmons in 2D or quasi-2D systems. Through advances in monochromation, electrons have also been recently used to probe optical phonons in bulk. In Fig. 4, we show the EELS probability for electrons with energies on the order of 100 keV traversing a polar monolayer. Because of the strong coupling between matter and LO phonons shown in Fig. 3,

one expects multiple LO phonon excitation to be possible. Thus, this effect must be taken into account in the EELS.

... (16)

The ability to probe low-loss and highly confined electromagnetic modes associated with 2D LO phonons in polar materials provides a new platform for nanophotonics in the mid- and far-infrared spectral range. The identification of the phonon polariton of bulk and thin-film geometries with the 2D LO phonon made in this manuscript may one to allow extend the rich phenomenology of optical phonons to nanophotonic applications. It also may lead to useful new ways to study LO phonons, arising from the fact that 2D LO phonons, unlike their 3D counterparts, have their electromagnetic energy extend a considerable distance from the material boundary. Due to the strong electromagnetic interactions between emitters and 2D LO phonons shown in this manuscript, it may be possible to design interesting new hybrid states of matter and phonons based on quantum electrodynamical strong coupling. The highly confined optical phonon waves in polar monolayers may also provide interesting new opportunities in near-field radiative heat transfer, in which it has been long known that thin-film surface phonon

polaritons play a critical role. An important avenue of future study would be the *ab initio* calculation of lifetimes of 2D LO phonons associated with three-phonon processes and electron-phonon interactions. It would be of great interest to study the prospects of techniques such as isotopic purification and cryogenic temperatures for reducing the decay of these 2D LO phonons.

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