Controlling Light, Heat, and Vibrations in Plasmonics and Phononics

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Plasmonic nanostructures have attracted considerable attention for their ability to couple with light and provide strong electromagnetic energy confinement at subwavelength dimensions. The absorbed portion of the captured electromagnetic energy can lead to significant heating of both the nanostructure and its surroundings, resulting in a rich set of nanoscale thermal processes that defines the subfield of thermoplasmonics with applications ranging from nanotechnology and nanobiology to optoelectronics. Recently, phononic nanostructures have started to attract attention as a platform for manipulation of phonons, enabling control over heat propagation and/or mechanical vibrations. The complex interaction phenomena between photons, electrons, and phonons require appropriate modelling strategies to design nanodevices that simultaneously explore and exploit the optical, thermal, and mechanical degrees of freedom. Examples of such devices are micro- and nanoscale opto-thermo-mechanical systems for sensing, imaging, energy conversion, and harvesting applications. Here, an overview of the fundamental theory and concepts crucial to the modelling of plasmo-phonon devices is provided. Particular attention is given to micro- and nanoscale modelling frameworks, highlighting their validity ranges and the experimental works that contributed to their validation and led to compelling applications. Finally, an open-ended outlook focused on emerging applications at the intersection between plasmonics and phononics is presented.

1. Introduction

Plasmonics is the field of photonics that studies the interaction of light (photons) with electrons at the interfaces between metallic structures and dielectrics. Essentially concerning the study of the Maxwell’s equations, its theoretical roots go back more than a 100 years to the beginning of the twentieth century.[1] However, owing to the recent improvements in nanofabrication and characterization techniques, it was only in the last decades that plasmonics emerged as a prolific area of applied optics. Phononics is the field of condensed matter physics that studies collective vibrational modes of matter (phonons) as means to carry energy (heat) and information (vibration and sound). Beginning with atomic scale models describing the lattice dynamics, its theoretical roots go back to the foundations of the field of condensed matter physics itself before the first half of the twentieth century[2,3]. Analogously to plasmonics, the ability to fabricate structures with sub-μm features is now opening possibilities for exploiting phonon propagation hence promoting a renewed interest in the phononic field. Even more importantly, the nowadays advanced micro- and nano-fabrication technology enables the actual realization of opto-thermo-mechanical nanodevices[4,5] where the interaction between photons, electrons, and phonons can be properly investigated and exploited.

Starting from the seminal work of Ritchie in 1957,[6] numerous studies have been performed on systems supporting plasmonic effects, such as metallic slits or perforated metallic films together with hybrid structures formed by metal and dielectric.[7] Plasmonic nanostructures have especially attracted a lot of attention for their ability to couple with light whose...
wavelength is much larger than the nanostructures dimensions,[8] importantly enabling an efficient localization of energy in small volumes well below the diffraction limit.[1] Another aspect related to plasmonic materials is their lossy characteristic which ultimately turns electromagnetic energy into heat.[9] While detrimental for some applications, controlled nanoscale heat generation can be a key enabler for many thermoplasmonic applications, as explored in the fast growing fields of nanomedicine,[10,11] nanobiology,[12] and nanochemistry.[13–16] In this scenario, thermoplasmonics[17] focuses on the possible strategies for an efficient heat generation while phononics[18] dedicates itself especially to the phonon manipulation.[19–21] Additionally, the fact that both thermoplasmonics and phononics ultimately harness the same kind of particle, results in a further push for the identification of structures or devices capable of exploiting the particle/wave dual nature associated to phonons.

The scope of this review is double fold: i) To provide a comprehensive description of the fundamental mechanisms underneath the photon–electron–phonon interaction together with the associated experimental advancements highlighting the role played by phonons in the optical, thermal and mechanical properties of nanosystems; ii) To elaborate about the key design parameters for conceiving and realizing future devices and experimental platforms at the intersection between plasmonics and phononics for thermal and optomechanical applications. Other review articles have provided interesting views on related subjects, for example, refs. [22,23] focused on applications of thermoplasmonics or ref. [24] which reviewed diverse thermal aspects of metal nanostructures. Here, in contrast, we pay particular attention to describing the physical processes and the conceptual frameworks to provide a helpful guide for new plasmo-phononics applications. In this regard, **Figure 1** schematizes the main connections linking the physical processes that are discussed in this review.

In Figure 1, light coupling with plasmonic nanostructures depends on photon-induced electronic transitions in which electron–phonon interaction can take part. In fact, light-induced electronic transitions ultimately determine the optical response of plasmonic nanostructures. Furthermore, the optical response of nanostructures, through Joule heating, can lead to a temperature increase (both of the electrons and of the lattice). The lattice temperature variation is associated to the excitation of thermal phonons, which can influence the heat transport properties of the nanostructure. In this respect, the heat transport management could hypothetically be realized through a phononic engineering approach[19] by designing phononic crystals to tailor the propagation of phonons. At the same time, a lattice temperature increase leads to a lattice volume expansion with consequent excitation of mechanical phonons. Additionally, the temperature increase and the mechanical structural changes can influence back the light-induced electronic transitions resulting in a modified optical response.

Throughout this review, characteristics of the processes where the phonons take part will be directly referred to the phonons themselves. Therefore, non-equilibrium and equilibrium phonons refer to phonons in non-equilibrium or equilibrium states, particle and wave phonons refer to the particle and wave representation of a phonon, coherent and incoherent phonons refer to the quantum mechanical property for a particle-like phonon to preserve, or not, its phase upon scattering and to exhibit, or not, wave-like interference. Similarly, thermal and mechanical phonons refer to phonons associated to different spectral ranges carrying energy that manifests as heat or sound, respectively. Optical and acoustic phonons refer to the dispersion branch and longitudinal and transverse phonons refer to the polarization of the phonons.

In this review these multiple interactions will be carefully explored and their tailoring, according to the desired application, will be discussed. Before delving into details of the plasmonics and phononics processes, we briefly introduce the background and definitions related to phonons and plasmons in Section 1.1. In Section 2, we shall analyze the energy transfer to

**Figure 1.** Schematic describing the two fields of plasmonics and phononics and their overlapping areas. The arrows indicate a unidirectional or bidirectional connection, representing how processes influence each other. The dashed connections represent effects normally disregarded in a first approximated analysis which may be crucial for accurate predictions or specific applications.
plasmonic structures upon interaction with light, how phonons influence this interaction and how the energy transferred to the structure eventually results in a lattice temperature increase. In Section 3, we shall explore the role of phonons in terms of heat transport both in metals and dielectrics, and discuss recent studies reporting strategies to manipulate heat propagation by controlling phonons. In Section 4, we shall provide a detailed analysis of the (indirect) energy transfer between light and phonons focusing on the phonon excitation mechanisms in metals. Finally, in Section 5, we shall propose an open-ended outlook envisioning applications on the verge of the two fields, plasmonics and phononics.

1.1. Background on Phonons and Plasmons

1.1.1. Phonons

Simply put, phonons are the quantum of vibration in solids. While the complete theory is discussed at length in classic books of solid state physics,[2,3,25,26] here we introduce optical, acoustic, longitudinal, and transverse phonons as they will be often referenced in the text. Briefly, in a solid, the atoms arrange themselves in an organized manner so that the overall interaction potential is minimized. If the atomic arrangement is a periodic translational repetition of a single unit cell leading to a long-range order, we refer to it as a crystal. The geometrical arrangement of the unit cell can be one of a limited number of geometrical forms known as Bravais lattice structures.[25] The arrangement of the atoms within the unit cell forms the basis which can be monoatomic (one atom) or polyatomic (two or more atoms). The crystal is thus composed of the repetition of an atomic basis in a spatially periodic lattice. The presence of vibrations in crystals can then be studied by describing the time-dependent positions of the atoms within the lattice and their interatomic forces. The most basic model considers a linear 1D chain of atoms where the interatomic forces are modeled by springs pulling the atoms together. In the simplest case the interatomic forces are considered to be harmonic (i.e., as in a harmonic oscillator, the interatomic force is typically feature large frequencies and small momenta given the large value of the speed of light) and are thus called optical modes. While in 1D the atoms can move only parallel to the mode wavevector, in 3D they can move either parallel, longitudinal modes, or perpendicular, transverse modes, to the wavevector. The direction of movement of atoms thus defines the mode polarization as either transverse or longitudinal. It follows that in 3D each wavevector is associated to three polarizations, one longitudinal and two transverse. The vibrational energy of the crystal is thus contained in an assembly of normal modes, also referred as lattice waves. Alternatively, the crystal can be seen as a collection of 3N harmonic oscillators given by N number of atoms oscillating in the three possible polarizations. From a quantum mechanical point of view, the total vibrational energy E of the solid can be derived by summing over all the wavevectors q and polarizations p, obtaining[25]

$$E = \sum_{q,p} (\omega_{q,p} + 1/2)\hbar\omega_{p}$$

where \(\omega_{q,p}\) is the mean number of phonons with energy \(\hbar\omega_{p}\). The number of phonons at a particular frequency represents the amplitude at which that mode of vibration is excited. The average number of phonons in a mode of frequency \(\omega\) in thermal equilibrium at temperature \(T\) is given by the Bose–Einstein distribution (exp \((\hbar\omega_{p}/k_{B}T) − 1\))−1, where \(k_{B}\) is the Boltzmann constant. Therefore, for a crystal at temperature \(T\), we can expect to find phonons with average frequency \(\omega_{p} = k_{B}T/h\) (=40THz at room temperature). We typically refer to thermal phonons if the average phonon frequency \(\omega_{p}\) is in the range 0.1THz – 100THz whereas mechanical phonons typically refer \(\omega_{p}\) of lower frequencies (i.e., kHz to GHz).[39] Additionally, we should note that the concept of phonon is classically linked with the existence of a lattice. However, in the quantum picture, the lattice has been replaced by a “volume”, filled by a “gas” comprised of phonons.[3]

In equilibrium, it is possible to define a relation between the lattice and the phonon gas thermodynamical quantities (e.g., temperature or heat capacity). However, it is more common to find those quantities associated with the word lattice.

1.1.2. Plasmons

Plasmons are collective oscillations of a medium free (conductive) electrons and their properties strongly depend on the utilized materials, structure shape and dimensions, number of involved particles and their mutual interaction. Plasmons can be excited and sustained in a plasmonic structure in the form of volume plasmons or surface plasmons. Volume plasmons correspond to longitudinal collective
oscillations of the material free electrons at frequency \( \omega_p \), which is known as plasma frequency. The plasma frequency is given by \( \omega_p^2 = n_e^2 e^2 / \varepsilon_0 m \), where \( n_e \) is the free electron density, \( e \) the electron charge, \( \varepsilon_0 \) the vacuum electric permittivity and \( m \) the electron effective mass. The plasma frequency expresses the rate at which electrons in a given material oscillate if displaced from their equilibrium position (for instance, by an external electric field). Volume plasmons can be excited by inelastic scattering of an electron in a metal film[6] and imaged through plasmon imaging techniques such as electron energy loss spectroscopy (EELS).[13] Being longitudinal oscillations, volume plasmons do not couple to external propagating transverse electromagnetic waves. On the other hand, surface plasmons (SP) can be excited at the interfaces between plasmonic and dielectric materials by interacting with electromagnetic fields under specific frequency (energy) and wavevector (momentum) matching conditions.[14] SPs can be further categorized into propagating surface plasmon polaritons (SPPs) or localized surface plasmons (LSPs) depending on the geometry of the plasmonic structure and the employed excitation strategy. Typically, SPPs are generated in extended substrates by coupling an external radiation through properly designed gratings patterned at the metal/dielectric interface.[15] SPPs can be utilized to propagate, guide, and focus electromagnetic radiation along a 2D surface.[16,37] SPPs have a hybrid nature consisting of light waves propagating in the dielectric medium, in immediate vicinity of the interface, accompanied by a correspondent collective electron oscillation, in immediate vicinity of the interface, inside the material. Figure 2a illustrates schematically a SPP on a planar interface. To excite SPPs, momentum and energy conservation need to be fulfilled. Figure 2b shows, represented by a dashed line, the ideal (lossless) SSP dispersion. A more realistic dispersion curve is, however, the one represented by the orange line which includes a damping term that will be detailed in Section 2.1. Clearly in Figure 2b there is a momentum mismatch between the (lossless) SPP branch and free space photons of the same energy (frequency). The mismatch can be addressed with multiple approaches such as Otto or Kretschmann prism coupled configurations,[14] grating couplings or subwavelength structures patterning.[14] The orange line in Figure 2b shows a continuous transition from the SPP dispersion branch into the upper high-energy radiative plasmon branch. The transition happens when losses in the metal become so large that, to satisfy the momentum mismatch, the wavevector of the SPP mode perpendicular to the interface turns from imaginary (evanescent field) to real (propagating field), effectively impeding further plasmon in plane propagation. In general, metallic losses cause the propagating SPP to gradually attenuate. In the case of an Ag film interface, which has reduced losses in the visible (compared with other plasmonic materials), propagation distances are in the range of 10–100 \( \mu m \) and increasing (toward 1 mm) for longer wavelengths (in the near-infrared).[38]

In metallic nanostructures smaller than the wavelength of the incident EM wave, due to geometrical constraints, modes of collective oscillation of the free electrons can be excited establishing a LSP. The lowest order mode is a dipolar mode where surface charge densities of opposite polarities accumulate at the particle edges (Figure 2c). The density of the induced charges depends on the polarizability of the particle which can be maximized at its localized surface plasmon resonance (LSPR). The dipolar LSPR is the lowest order resonance and other higher-order LSPRs are associated with multipolar modes at higher frequencies. The charge density accumulation at the edges induces an electric field in the proximity (inside and outside) of the nanoparticle surface. The LSP leads thus to a local electric field enhancement with maximum in the dielectric medium in the immediate vicinity of the surface, offering key applications in sensing, nanoscale heating, or plasmon-photocatalysis.[34,36]

Predicting and engineering the plasmonic properties for harnessing SPPs or LSPs often requires numerical calculations. In fact, analytical solutions to the governing equations exist for a reduced number of simple geometries. Importantly, current synthesis and fabrication techniques allow to control materials, shape, and size of nanostructures that yield experimental results in remarkable accordance with theoretical models (Figure 2d.e).[28,39] Therefore, rigorous light–matter interaction modeling becomes crucial to design and engineer advanced optical nanodevices, especially in view of opto-thermal coupling phenomena. In this regard, in the next section, we outline the theoretical approach to properly model the interaction between EM fields and dissipative plasmonic structures.

2. Light Interaction in Plasmonic Nanostructures

Plasmonic systems have been attracting a wide interest across different fields mainly due to their ability to concentrate electromagnetic energy down to volumes well below the diffraction limit thus reaching nanoscale dimensions.[40,41] This characteristic has led to a variety of applications, embracing spectroscopy,[42] molecular sensing,[43] photovoltaics,[44,45] nanophotonics,[46] nanochemistry,[15,16,47] medical applications,[50,55–50] and desalination devices.[51–53]

2.1. Light Coupling in Plasmonic Nanostructures and Dissipative Loss

The interaction between light (described as a propagating EM wave with electric field \( \mathbf{E} \) and magnetic field \( \mathbf{H} \)) and a nanostructure is classically governed by Maxwell’s equations. In particular, assuming \( |\mathbf{E}| \ll \exp(-i\omega t) \), where \( \omega \) is the angular frequency of incoming light, the electric field distribution can be computed from the Helmholtz wave equation, as derived from the Maxwell’s equations:[54]

\[
\nabla \times \mu_r^{-1} (\nabla \times \mathbf{E}) - \left( \frac{\omega^2}{c^2 \varepsilon_0} \right) \varepsilon_r(\omega) \mathbf{E} = 0
\]

(1)

where \( \mu_r \) is the magnetic permeability and \( \varepsilon_r(\omega) \) is the (complex) relative permittivity of the medium as function of the angular frequency. In the following we assume non-magnetic materials, \( \mu_r = 1 \).

2.1.1. The Permittivity

The interaction between light and the plasmonic material induces electronic transitions due to photon absorption. An accurate
description of the optical response of a medium relies on a precise modeling of its electric permittivity $\varepsilon$. In the case of metals (in particular noble metals), the permittivity is decomposed in two contributions corresponding to electronic transitions within the conduction band, the intraband contribution, often described by the Drude model, $\varepsilon_D(\omega)$, and transitions from inner bands to the conduction band, the interband contribution, $\varepsilon_{ib}(\omega)$. We can write the permittivity as $\varepsilon(\omega) = \varepsilon_D(\omega) + \varepsilon_{ib}(\omega)$.
2.1.2. The Intraband and Interband Contributions

The intraband contribution is often described following the classical Drude model.[55] The Drude model describes a “gas” of free electrons interaction with an oscillating electric field with time dependence exp (−iωt). The correspondent permittivity term is ε0(ω) = 1 − a2/ω2 + iγω) where γ is the damping coefficient, in units of angular frequency, which represents a dissipative scattering rate to phenomenologically account for the possible electronic scattering processes: electron–electron, electron–phonon, electron-impurity, and electron-surface scattering.

The interband contribution cannot be classically derived since it originates from direct electronic transitions between d and s bands (see, e.g., Figure 2f in red). A rigorous approach can be introduced phenomenologically as a scattering rate comprising the involved quantum phenomena, is based on approximating the interband contribution by a classical model where interband transitions are described by Lorentz oscillators which mimic the photon absorption between two energy levels yielding to εω(ω) = ∑ fj(ωj − ω′ − iαj) with a number m of oscillators each with frequency ωj, strength fj and lifetime 1/Γj.

The combination of the interband (Lorentz) and intraband (Drude) terms gives the, so-called, Drude–Lorentz model. The practical utility of the Drude–Lorentz model relies on a satisfactory parametrization of an arbitrary number of Lorentzian oscillators that matches the experimental permittivity (obtainable, for instance, through thin-film ellipsometry measurements[30]). Employing a customized fitting procedure, Rakić et al.[30] provided the Drude–Lorentz parametrization of several metals (Ag, Au, Cu, Al, Be, Cr, Ni, Pd, Pt, Ti and W). Figure 2d illustrates a good matching between simulation results employing the Drude–Lorentz model and experimental data.[28,29]

The damping coefficient γ in the intraband contribution was introduced phenomenologically as a scattering rate comprising electron–electron, electron–phonon, electron-impurity, and electron-surface scattering. In sufficiently pure and homogeneous materials, electron-impurity scattering can be neglected.[56] Regarding the remaining components, a more physical description of the damping can be obtained through a microscopic view of the electronic scattering processes. In particular, the contributions of electron–electron and electron–phonon scattering processes to the damping coefficient can be microscopically analyzed through electronic intraband transitions.

2.1.3. Damping Coefficient and Phonon Contribution to Damping

Microscopically, an electronic intraband transition is expressed by the absorption of an incoming photon by an electron assisted by the scattering with a second electron or phonons (thereby causing absorption or emission of phonons) in order to conserve energy and momentum. In a simplified band-structure diagram for metals, those processes are represented in Figure 2f in orange (electron–electron) and green (electron–phonon).

Intraband electronic transitions assisted by electron scattering, as first studied by Gurzhi,[57] can be described by the temperature and frequency-dependent electron–electron scattering rate γ−→(ω, T) = γ−→(T) 1 + (hω/2πkT) and for frequencies in the infrared and optical and from low to room temperatures, where Γ is the averaged scattering probability, Δ is the dimensionless fractional umklapp scattering, EF is the Fermi energy, and kT is the Boltzmann constant. Values for Γ and Δ are available for noble metals in ref. [56].

Intraband scattering between electrons and phonons is a complex aspect that reflects the subtleties of the microscopic interaction between electrons and vibrations of the lattice. A relatively simple expression of the scattering rate of electrons by phonons γ−→ can be obtained as the lowest order variational solution to the Boltzmann equation for electron transport[61–63]

$$\gamma_{\rightarrow\rightarrow}(\omega, T) = 4\pi \int_0^{\infty} \frac{(\hbar\omega/kT)\alpha^2F(\omega)}{[\exp(h\omega/kT) - 1]} d\omega (2)$$

where hω is the phonon energy and αF(ω) is the electron–phonon spectral coupling function (in superconductors, it is linked to the Eliashberg electron–phonon coupling function[61,62,64]). Equation (2) assumes that phonons are in an equilibrium state described by the Bose–Einstein distribution function [exp(hω/kBT) − 1]−1 and that available electrons are located in the vicinity of the Fermi surface.[61,62] The function αF(ω) contains all of the information on the electronic structure, the phonon spectrum, and the electron–phonon coupling with an arbitrary phonon spectrum and an arbitrary Fermi surface.[64] In the absence of detailed knowledge about the electronic structure, phonon spectrum and electron–phonon coupling, it is still possible to make educated guesses concerning the spectral behavior of αF(ω). For example, assuming a typical Debye dispersion and a spherical Fermi surface, αF(ω) ∝ ω3 when considering only longitudinal phonon coupling by Normal scattering processes[61,62] (momentum conservation with G = 0). Detailed account on the exact calculation of the electron–phonon spectral coupling function can be found, for example, in ref. [62].

For plasmonic applications in the near-infrared and visible frequencies at room temperature, it has been shown,[65] assuming electron scattering in a spherical Fermi surface, a Debye phonon spectrum and neglecting umklapp scattering processes, that the scattering rate γ−→ can be described by

$$\gamma_{\rightarrow\rightarrow} = \gamma_0 \left[ \frac{2T^5}{5} \pi^5 \int_0^{\Theta_0} \frac{4z^4}{e^{z} - 1} dz \right]$$

where γ0 is a material dependent constant (e.g., 0.07 eV for Au in ref. [60]) and ΘD the Debye temperature. This expression is commonly used in studies related to the influence of temperature on the optical response of plasmonic materials, for example, refs. [29,60]. A detailed account of the derivation and expressions for other frequency and temperature ranges is present in ref. [66].

A more rigorous approach to obtain the scattering rate γ−→ is given by the Fermi Golden Rule for the scattering of an electron in a state k, to a state k′, by a phonon of wavevector q and polarization p. This makes the scattering rate dependent on...
the electronic bandstructure and phonon distribution, unfortunately both difficult to obtain experimentally. The calculation of the matrix element for this transition (for a detailed account see refs. [3,67]) contains a sum over all reciprocal vectors $\mathbf{G}$ with interaction term $\xi_\mathbf{q} \mathbf{q} \cdot (\mathbf{q}_p + \mathbf{G})$ between the unit vector of ion displacements $\xi_\mathbf{q}$ and the modes $\mathbf{q}_p$. A typical approach is to consider the long-wavelength limit (small $\mathbf{q}$) and carry the calculation of the matrix element through perturbation theory, neglecting the summation over $\mathbf{G}$, except for a single $\mathbf{G}$.\[68]\] For the transition matrix element to be different from zero (and thus a transition to be allowed), we need $\xi_\mathbf{q} \parallel (\mathbf{q}_p + \mathbf{G})$. It follows that in electron–phonon scattering with electrons in a spherical Fermi surface (a good approximation in noble metals for example), there are no Normal scattering processes ($\mathbf{G} = 0$) for the transverse phonon modes, as $\xi_\mathbf{q} \perp \mathbf{q}_p$. This motivates the common assumption that electron–phonon interaction is dominated by scattering between electrons and longitudinal phonons\[69–72\]. However, transverse phonon modes can give rise to umklapp scattering processes ($\mathbf{G} \neq 0$) or participate in Normal scattering processes if the Fermi surface is not spherical (Fermi surfaces of some metals can be in fact far from spherical\[25\]). These simplifications ultimately allow to calculate the matrix element for an electron in a state $\mathbf{k}_1$ to a state $\mathbf{k}_2$ by scattering with longitudinal phonons. Reciprocally, the matrix element is the same for scattering of longitudinal phonons by electrons, yielding to a correspondent modification in the energy levels of the electronic distribution (electrons) due to strain (longitudinal phonons) in solids. This strain induced electronic level shift is at the root of the deformation potential theory\[73\]. As pointed out first by Bardeen and Shockley\[74\] and expanded by Herring and Vogl\[75\] this theory is especially well-suited for semiconductors and insulators where electrons possess low energy (with respect to the Fermi level) and electron and phonon wavelengths involved are long. In metals, a properly treated electron–phonon interaction\[67,75\] provides an interesting connection element between plasmonics and phononics.

For completeness, we note that in nanostructures of dimensions below the (material-dependent) electron mean free path, the effects of electron-surface scattering should be also taken into account. This can be done, for example, by introducing an additional damping term $\gamma_{\text{scat}} = AV_v/t_\text{off}$ where $A$ is a dimensionless parameter describing the surface scattering mechanism, $V_v$ is the electron Fermi velocity in the material and $t_\text{off}$ is the reduced mean free path of the electron (see ref. [29] for details). Its relative importance with respect to $\gamma_{\text{scat}}$ is $\gamma_{\text{scat}}$ and $\gamma_{\text{scat}}$. These cross sections can in general be computed numerically or, in a few cases (e.g., spherical or cylindrical particles), analytically with Mie theory\[36\].

2.1.4. Energy Absorption and Scattering in Plasmonic Nanostructures

Once the material permittivity is correctly modelled, the optical response of a nanostructure can be obtained by solving Equation (I) with the desired geometry and dimensions, obtaining the electric field $\mathbf{E}$ and magnetic field $\mathbf{H}$ distributions inside and outside the structure. From the calculated field distributions, the time-averaged scattered ($Q_{\text{scat}}$) or absorbed ($Q_{\text{abs}}$) powers are given by\[83\]

\[
Q_{\text{scat}} = \frac{1}{2} \text{Re}\left\{ \int \int \int [E_\text{inc} \times H_\text{inc}] \cdot \mathbf{n} \, dS \right\}
\]

(4)

\[
Q_{\text{abs}} = \frac{1}{2} \text{Re}\left\{ \int \int \int [E_\text{tot} \times H_\text{tot}] \cdot \mathbf{n} \, dS \right\}
\]

(5)

where we have used a scattering field formulation\[36\] with $E_\text{tot} = E_\text{inc} + E_\text{scat}$ and $H_\text{tot} = H_\text{inc} + H_\text{scat}$ with the subscripts inc, scat, and tot referring to incident, scattered, and total field, $S$ is a surface enclosing the nanoparticle, and $\mathbf{n}$ is a unit vector normal to the surface $S$ and pointing outward.\[83\] The vectorial quantity $S = E_\text{tot} \times H_\text{tot}$ represents the Poynting vector which specifies the magnitude and direction of the EM energy flux\[34\].

Considering an incoming light of intensity $I_0$, the absorption and scattering cross sections are defined as

\[
\sigma_{\text{abs}} = \frac{Q_{\text{abs}}}{I_0}
\]

(6)

\[
\sigma_{\text{scat}} = \frac{Q_{\text{scat}}}{I_0}
\]

(7)

with extinction cross section given by $\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}}$. These cross sections can in general be computed numerically or, in a few cases (e.g., spherical or cylindrical particles), analytically with Mie theory\[83\].

2.1.5. Energy Dissipation into Heat

The absorbed power $Q_{\text{abs}}$ in Equation (5) represents the volume integral of the power density dissipated as described by the Joule effect given by\[54\]

\[
q_{\text{abs}} = \frac{1}{2} \text{Re}\left\{ \mathbf{J} \cdot \mathbf{E} \right\}
\]

(8)

where $\mathbf{J}$ is the electric current density. Under monochromatic illumination, we can write

\[
Q_{\text{abs}} = \frac{\omega}{2} \text{Im}\{\varepsilon\} \int \int |\mathbf{E}|^2 \, dV
\]

(9)

where $\varepsilon$ is the permittivity of the nanoparticle, $|\mathbf{E}|$ is the total electric field amplitude, and the integral is carried on the nanoparticle volume. The absorbed power $Q_{\text{abs}}$ is also called the electric dissipative loss sometimes found in literature.\[76\] Following Equation (8), the dissipative loss is directly related to the imaginary part of the permittivity, $Q_{\text{abs}} \propto \text{Im}\{\varepsilon\}$. Dissipative losses within nanoparticles are accompanied by heat transfer via conduction, radiation and, in a fluid environment, convection.\[77\] For now we simply underline the connection between dissipative losses and heat generation and will detail the obtained temperature distribution in Section 2.2.

Electromagnetic power dissipation in nanostructures is particularly relevant if the particle dimensions are much smaller than
the wavelength of the incident radiation (e.g., for nanospheres of radius $R < 50 \text{nm}$ excited in the visible or near-infrared), where the interaction with light can be treated in the Rayleigh approximation.\(^8\) In this case, the absorption cross section (directly proportional to the absorbed power, Equation (6)), $\sigma_{\text{abs}}$ in the Rayleigh approximation becomes larger than $\sigma_{\text{ext}}$.\(^8,34\) In Figure 2g,h, we illustrate the absorption of EM energy in nanospheres of different radius by mapping the EM energy flux (Poynting vector). Red lines indicate the separation between flux lines penetrating the particle from those bypassing it.\(^31\) As the nanosphere radius is shrunk, Figure 2h shows the EM energy funneled to the nanoparticle noticeably increases by several orders of magnitude.

### 2.1.6. High- and Low-Loss Materials

Heat dissipation in nanostructures can be enhanced or minimized, depending on the application. Typically, in applications dealing with light transmission, manipulation, detection, or harvesting, low dissipative loss is preferred.

To compare the dissipation performances of various materials, the quality factor, or Q-factor, is often introduced. Among the possible definitions for the Q-factor, we follow ref. [78] yielding $Q = \frac{-\alpha d Re[\varepsilon]}{d \omega} / 2 \Im[\varepsilon]$. Thus, as $Q \propto 1/\Im[\varepsilon]$, high Q-factors are usually associated with low dissipative losses. In Figure 2i, Q-factors are represented as function of frequency for different materials. From Figure 2i, we infer Q-factors of semiconductors and metals are comparable while polar dielectrics exhibit higher Q-factors at longer wavelengths. The large Q-factors of polar dielectrics arise in the Reststrahlen range, defined by the conditions $\Re[\varepsilon] < 0$ and $\Im[\varepsilon] \ll -\Re[\varepsilon]$, typically located in the mid-infrared. The permittivity of polar dielectrics in the Reststrahlen range is dominated by light interaction with optical phonons instead of electrons.\(^32,79\) Similarly to SPPs, through a proper modeling of the permittivity,\(^79\) surface phonon polaritons (SPhPs) can be described as a solution to the Maxwell’s equations at material interfaces formally identical to SPPs but physically interpreted as a joint oscillation of the EM wave and the optical phonons at the interface of the polar dielectric.\(^80\) Similarly to SPPs, SPhPs excitation is achieved by energy and momentum conservation, in the Reststrahlen range. Further, similarly to LSPs, localized phonon polaritons can give rise to resonant excitations in nanoparticles of semiconductors or polar crystals\(^81\) illuminated at mid-infrared frequencies. The parallel between phonon and plasmon polaritons has been highlighted, for example, in recent imaging studies\(^82\) reporting EELS spectral maps of MgO (phononic) nanocubes with resonances in the meV and of metallic (plasmonic) cubic nanostructures with resonances in the eV range shown in refs. [83,84]. In this sense, SPhPs enable low loss “plasmonic” and nanophotonic applications in the mid-infrared.\(^32,81\) The interaction between SPP and SPhPs has also been investigated in SPP-SPhPs hybrids\(^85\) (see Section 5 for application examples). Although SPP-SPhPs are fundamentally at the intersection between plasmonics and phononics, the interaction (which relies on optical phonons for the phonon polaritons) does not in general gives rise to considerable heat (as it is more commonly the case for plasmon polaritons) and their underlying physics is out of the scope of this work. The interested reader is referred to refs. [32,86,87] for further details. In addition to the research efforts targeted at harnessing phonon polaritons for low dissipation nanophotonics, a great effort is devoted to the continued search for new plasmonic materials fueled by the desire of avoiding losses as, for example, reported in refs. [79,88,89].

### 2.2. Nanosources of Heat and Thermoplasmonics

One approach to exploit plasmonic systems is however to embrace the existence of losses and utilize plasmonic nanostructures as controllable nanosized sources of heat. This is the concept at the base of the thermoplasmonics field.\(^37\) The concept has been used with great success in nanomedicine for example to kill cancer cells.\(^49,50\)

#### 2.2.1. Thermoplasmonics

Typical thermoplasmonic effects arise when illuminating a single or an ensemble of metallic nanoparticles with a laser in order to generate heat and locally raise the particle’s and medium's temperature.\(^91–93\) Different regimes can be identified depending on the laser intensity and laser pulse duration. Thermoplasmonics applications often employ continuous wave (CW) illumination which allows the calculation of the temperature increase through a steady-state analysis,\(^39\) while ultrashort pulsed lasers can give rise to additional interaction phenomena at different timescales.\(^94\) In the latter case, pump-probe experiments are used to study the fundamental processes of energy transfer in metals and metallic nanoparticles. We briefly describe pump-probe energy transfer using the scheme in Figure 3a before providing more details in Section 4.1. The pulsed illumination of a metallic nanoparticle initially results in the excitation of a non-equilibrium electronic population (also referred as hot-electrons\(^95\)). These excited carriers relax through scattering with electrons, phonons, impurities, and the nanostructure’s surface, resulting first in a high electronic temperature, after approximately few ps, and, eventually in a lattice temperature increase, in $\approx 10–100$ ps. Finally, on a longer time scale, typically $\approx 100$ ps, the electronic and lattice temperatures are sensibly the same resulting in overall temperature increase of the particle and of the surroundings due to heat propagation.\(^96\) It is the electron–phonon scattering that provides the energy transfer channel from the high temperature electrons to the lattice leading to its temperature increase (see Section 4.1 for details). If the energy transferred is large enough, it can eventually cause a phase transition leading to nanoparticle melting.\(^97,98\) In steady-state, electron and lattice sub-systems are characterized by basically the same temperature, which allows the convenient definition of a single nanoparticle temperature $T$ simplifying the problem considerably.

Concerning the heat transfer processes, in plasmonic nanostructures at room and low temperatures heat conduction is typically the dominant heat transport mechanism.\(^11,77\) For heat conduction, the thermodynamical energy conservation equation describes the balance between the change in thermal energy density of the system $\partial u/\partial t = ρ_c c_P \partial T/\partial t$, the heat source density (from dissipation of EM energy) $q_{\text{abs}}$ and the flow across
the boundaries of the thermal energy current density given by the Fourier law $j = -\kappa \nabla T$. As result, the well-known heat diffusion equation is written as:

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + q_{abs}$$

Equation (10)
can be calculated\textsuperscript{[9,94,99]} by cancelling the temporal dependence of the temperature in Equation (10)

\[-\nabla \cdot (\kappa \nabla T) = q_{\text{abs}}\]  

(11)

To illustrate the photo-induced temperature increase, we consider a typical thermoplasmonic system\textsuperscript{[92,94,99]} a gold sphere of radius \( R \) immersed in water. We are interested in calculating the steady-state temperature profile under CW illumination with typical limit condition of a background room temperature at a distance far away from the heated sphere. Fluid convection that could potentially influence the calculated temperature profile around the plasmonic nanoparticle has been shown to have a negligible effect for moderate temperature increase and single plasmonic particles of small dimensions and is thus disregarded\textsuperscript{[104,105]}. Since water is a non-absorbing medium, the heat conduction equation in water is simply the Laplace equation \(-\nabla \cdot (\kappa \nabla T) = 0\), resulting in a 1/r dependence in a spherical geometry (see Equation (13)). As \( \kappa_{\text{gold}} \gg \kappa_{\text{water}} \), heat flows much faster inside the nanoparticle than in water, leading to a uniform temperature inside the nanoparticle. From an energy conservation perspective the power going through the particle interface at \( r = R \) must be equal to the power delivered to the particle \( Q = J - \kappa_T \cdot dS \), resulting in a temperature increase \( \Delta T_0 = \frac{Q_{\text{abs}}}{4\pi\kappa_{\text{water}} R} \). The temperature spatial profile is (in the uniform temperature approximation) given by\textsuperscript{[97,92]}

\[\Delta T(r) = \Delta T_0 \frac{r}{4\pi\kappa_{\text{water}} R} \quad r < R \]  

\[\Delta T(r) = \Delta T_0 \frac{R}{r} \quad r > R \]  

(12)  

(13)

where the \( Q_{\text{abs}} \) can be obtained from Equation (5). In Figure 3b, we show the temperature profile for a nanosphere immersed in water in the case of CW illumination in the vicinity and inside a nanosphere. If the heating source is non-spherical, numerical simulations are usually required\textsuperscript{[12,108]} Nevertheless, under the uniform temperature approximation, Baffou et al.\textsuperscript{[92]} proposed a fitting procedure for rods, discs, ellipsoids, and tori to obtain the uniform temperature rise of the particle by describing the particle as spherical with an effective radius accounting for the difference in shape. Details and closed-form expressions for rods, discs, ellipsoids, and tori can be found in ref. [92].

2.2.2. Nanoscale Temperature Measurement Techniques

The experimental measurement of temperature at the nanoscale is challenging, especially if the temperature spatial profile is sought. In fact, the latter is regarded as an open problem where further developments of existing or new techniques are expected\textsuperscript{[17]} Nevertheless, several micro-scale thermal imaging techniques recently became available and we refer to the use of infrared cameras\textsuperscript{[107,108]} temperature-dependent photoluminescence emission microscopy\textsuperscript{[109]} temperature-dependent thermographic phosphorescence microscopy\textsuperscript{[110]} fluorescence polarization anisotropy microscopy\textsuperscript{[103]} nanodiamond nitrogen vacancy centers\textsuperscript{[111]} thermal-induced refractive index variation of the surrounding medium\textsuperscript{[112]} temperature-dependent Raman spectroscopy based techniques\textsuperscript{[111,114]} temperature induced shift of plasmon peaks in EELS spectra (named plasmon energy expansion thermometry [PEET])\textsuperscript{[115]} and scanning thermal microscopy (SThM)\textsuperscript{[116]} These techniques are based on a variety of physical phenomena that will not be detailed here (the interested reader is referred to the respective references) and differ in their spatial, temporal, and temperature resolution (a comparative account is provided, for instance, in ref. [117]). Each technique should be carefully selected depending on the specific application. Here, we illustrate two recent thermal imaging results in Figure 3c,d. Figure 3c shows the experimental results of Baral et al.\textsuperscript{[100]} obtained through a scanning optical probe thermometry technique based on measuring the photoluminescence of a laser-trapped erbium oxide nanoparticle to obtain the absolute temperature of optically excited Au nanodots with a spatial resolution limited by the size of the trapped nanoparticle. In particular, Figure 3c(iii) shows the measured temperature profile has a Gaussian shape, which can be interpreted as the convolution of the point spread function of the scanning probe and the theoretical temperature profile (e.g., Figure 3b). Figure 3d shows the experimental results obtained with fluorescence microscopy based on molecular polarization anisotropy obtained by Baffou et al.\textsuperscript{[101]} These results suggest the suitability of the thermoplasmonic theoretical analysis described above.

2.2.3. “Non-Linear” Control of Temperature Rise

The increase of temperature in nanostructures also results in the change of the temperature-dependent damping coefficient \( \gamma \) (see, e.g., Equation (3)) leading to the collateral effect of a change in permittivity \( \Delta \varepsilon \) which consequently influences the interaction with light by shifting and broadening the extinction resonance\textsuperscript{[29]} This “non-linear” (NL) approach to thermoplasmonics simulation was shown to be necessary in order to avoid substantial error in the calculation of the optical and opto-thermal response of plasmonic nanostructures\textsuperscript{[102]} (Figure 3e), Si and Ge dielectric nanoresonators\textsuperscript{[118]} and graphene\textsuperscript{[119]} Alabastri et al. further showed in ref. [103]. Figure 3f, that photothermal non-linearities can be used to control light–heat conversion in rod-like nanostructures with different aspect ratios. In particular, it was found that, for a given metallic nanoparticle, there is a value of the intraband dissipation term, \( \gamma = \gamma_{\text{amb}} \), for which the total heat dissipation in such nanoparticle is maximized. In the case of relatively large aspect ratio metallic rods, this value is directly proportional to the square of the fundamental (dipolar) plasmon resonance of the antenna-like nanostructure being considered \( (\gamma_{\text{amb}} \propto \omega_{\text{res}}^2) \). Interestingly, for mid-IR resonant wavelengths, the typical value of \( \gamma_{\text{amb}} \) that maximizes absorption, is very close to its room temperature value \( \gamma_{\text{amb}} = 53 \text{ meV} \). Since the value of \( \gamma \) depends on temperature (approximately in a linear way, at least for temperatures larger than \( \approx 200 \text{ K} \)), one can design rod-like nanostructures such that i) \( \gamma_{\text{amb}} > \gamma_{\text{max}} \) or ii) \( \gamma_{\text{max}} < \gamma_{\text{amb}} \). By illuminating these nanostructures at their fundamental resonance, electromagnetic dissipation will induce a temperature increase that, depending on condition i) or ii),
will increase or decrease further dissipation, respectively. Of particular interest is case ii) that induces a negative photo-thermal feedback by lowering the dissipation rate with the increase of temperature, therefore stabilizing the opto-thermal response. Figure 3f shows this experimentally demonstrated phenomenon for the case of metallic surfaces patterned with low- (L-AR) and high- aspect ratio (H-AR) antennas resonating at $\approx$3.2 $\mu$m and $\approx$13 $\mu$m, respectively. L-AR antennas were designed to feature $\gamma_{\text{max}} > \gamma_{\text{amb}}$ (case (i)) and, in fact, they exhibit an increasing absorption (decreasing reflectivity) with increasing temperatures. The opposite effect is achieved in the case of H-AR patterns. Dissipation rates increasing or decreasing by 20% and 30% for the two cases have been achieved in within a temperature range spanning from $\approx$200 K to $\approx$500 K. This photothermal positive or negative feedback can be exploited to accelerate or decelerate heating phenomena in different type of nanostructures, depending on the intended application.

These thermoplasmonic studies highlight strategies for controlling the heat generation in metals at the nanoscale using light. Once heat has been generated, one may be interested in managing such heat by controlling its propagation both in the metal and in its surrounding environment (i.e., dielectrics or semiconductors). Macroscopically, the heat transport depends on the thermal properties of the involved media, as can be studied using the diffusion equation, Equation (10). Microscopically, heat propagation depends on the transport mechanisms of electrons and phonons. In Section 3, we outline the heat transport mechanisms in nanostructures, analyzing the role played by phonons in those mechanisms according to recent studies and how they can be used to effectively enable the thermal design of nanostructures.

3. Heat Transport and Phononics

The manipulation of thermal transport at the nanoscale is crucial to improve the operation of nanodevices in applications ranging from microelectronics to optoelectronics to energy harvesting and biomedical devices. Thermal transport in these devices depends on the transport processes of the heat carriers (i.e., electrons and phonons). Given the complexities associated with thermal processes, rigorous modeling is necessary to accurately describe the overall thermal transport and enable the thermal design of nanodevices. Thermal modeling strategies need to be adapted to the system under consideration: the simplest strategy to model thermal transport considers the solid media as a continuum and employs macroscale equations that allow to obtain the physical variables describing the system (i.e., temperature and heat flux); a microscopic approach considers the solid media as an ensemble of individual atoms (or molecules) and describes their microscopic motion and interactions by solving the equations describing the dynamics of the ensemble (e.g., Newton’s second law in molecular dynamics and lattice dynamics). Schrödinger equation in first-principles density functional theory (DFT) can also be employed for a more rigorous approach. A question of major importance for the modeling and management of heat in nanostructures (e.g., plasmonic nanoparticle) and its surrounding environment (e.g., semiconductor or insulator) is: what is the most suited thermal modeling strategy that should be considered to describe heat transport at different scales? By analyzing transport in different space and time scales, both in metals and semiconductors/insulators, with special attention to the role played by phonons for transport in different materials and scales, by the end of this section we provide a summary of the answer, taking into account its practical implementation.

3.1. Heat Transport in Nanostructures

Macroscopically, heat conduction in solids is commonly described by the classical conduction theory introduced in Equation (10), where the Fourier law is considered. According to the Fourier law, a heat current flow $j$ is proportional to the temperature gradient through a (material-dependent) thermal conductivity coefficient $\kappa$.

$$j = -\kappa \nabla T \quad (14)$$

Microscopically, heat conduction is described by the transport of heat carriers (electrons or phonons) influenced by external interactions (e.g., external fields), internal diffusion processes and carrier scattering events. The scattering events define a mean free path for heat carriers $\ell$. If the dimensions of the nanostructure are larger than the carrier mean free path, the transport is defined as diffusive. Complementary, if dimensions are on the order of, or smaller than the heat-carrier mean free path, transport is defined as non-diffusive. We note that the macroscopic Fourier law in Equation (14) implicitly assumes diffusive carrier transport in the microscopic view. We now discuss its validity and use at micro- and nanoscale before exploring a more general modeling framework (the Boltzmann transport equation [BTE]).

3.1.1. Breakdown of the Fourier Law at Micro- and Nanoscale Dimensions

With the sub-micron dimensions of current technology of the order of, or smaller than the heat-carrier mean free path, the use of Fourier law is questionable. For instance, it has been shown that Fourier law predicts lower temperatures than the experimentally observed temperatures at hotspots generated in transistor junctions. This result is a consequence of the fact that transport by ballistic carriers gives an important contribution to heat transport in the non-diffusive regime. As the dimensions are shrunk, Majumdar and Chen have shown that, by modeling the carrier transport via the BTE, an increasingly important ballistic carrier contribution to heat transport leads to a breakdown of the Fourier law and thus of the concept of thermal conductivity in a conventional sense. In particular, refs. show that significant differences between the BTE and the Fourier law predictions for temperature and heat flux arise when the feature dimensions approach the heat carrier (in this case, phonon) mean free path. We should note that in the intermediate regime between ballistic
and diffusive transport, the transport is neither ballistic nor diffusive. In this intermediate regime some texts refer the transport as quasi-ballistic,[134] quasi-diffusive,[131] or ballistic-diffusive.[133] In this review, we adopt the later naming for this intermediate regime, but we advert that the naming is also associated to the general model, by Chen,[132,133] describing the transport in both ballistic and diffusive regimes.

In the limit where the nanostructure dimensions are much smaller than the mean free path, the transport is regarded as purely ballistic. In this limit, the ballistic carrier travels freely in straight lines and thus can be described in analogy to photon transport as radiation transport.[129] In this case, heat (energy) is transferred from one point to the other via ballistic carriers, without establishing a temperature gradient between the two points, and therefore a thermal conductivity cannot be defined in a conventional sense.

The breakdown of the Fourier law is schematically depicted in Figure 4a where a visualization of the heat carrier transport in a thin film is provided in diffusive (Figure 4a(i1)) and non-diffusive (Figure 4a(ii2)) regimes together with the associated temperature and heat flux profiles (Figure 4a(ii1) and (ii2)) along the direction perpendicular to the interfaces. The temperature and heat flux profiles in diffusive and non-diffusive regimes (Figure 4a(ii1) and (ii2)) have been subject of rigorous calculations of heat transport across a thin film based on the BTE.[133] The calculation result[133] shows that, in a thin film smaller than the heat carrier mean free path, a temperature gradient cannot be established along the direction perpendicular to the interfaces (in a similar fashion to the schematic of Figure 4a(ii2)), as opposed to the Fourier law predictions which would feature a well established temperature gradient. To cope with the breakdown of the Fourier law, Majumdar[129] and Joshi and Majumdar[135] derived, starting from the BTE, a radiative transfer equation which can be applied to both diffusive and ballistic transport (later expanded by Chen[132,133]). Refs. [129,135] radiative transfer equation bears similarities to a photon radiative transfer equation.[124]

Another approach to cope with the breakdown of the Fourier law at the nanoscale is to employ a fully atomistic first principles theory that accurately captures heat transport. However, first principles simulations require long computing times and advanced computational resources and are thus currently

Figure 4. a) Breakdown of the Fourier law at the micro- and nanoscale. ℓ is the mean free path and h is the thickness of the thin film. When h ≫ ℓ in (i) the transport is mainly diffusive and the Fourier law remains valid, establishing a temperature gradient within the film as evidenced by the linear temperature profile (ii) across the film. The breakdown of the Fourier law is evident in the case (ii1) and (ii2) where h ≈ ℓ and there is a strong contribution from ballistic carriers to heat transport. b) Phonon dispersion relation of Si with experimental data, group velocity of optical phonons around q = 0 point annotated; colors refer to optical (blue) and acoustic (red) branches. Adapted by permission. Copyright 2005, Springer Nature. c) Si bulk thermal conductivity as function of temperature, κ(T), showing the dominant mechanisms. Data from ref. [137]. d) Effective thermal conductivity of the embedding medium of a sphere of radius R as function of the size parameter R/ℓ, with mean free path ℓ in the medium around the particle (modelled following ref. [130]), with depicted transport regimes (color highlights diffusive vs non-diffusive, dashed lines roughly indicates the ballistic, ballistic-diffusive, and diffusive regimes).
limited to modestly small simulation domains of a few nm.\[138,139\] As the heat carrier mean free path is typically in the 10–100 nm scale,\[140\] the BTE is the common approach to model micro- and nanoscale heat transport.\[129-133,135,136\]

In the following, we outline the contributions to the most general form of the BTE and conceptually list solutions to the BTE that are relevant to heat transport without delving into the mathematical details; a comprehensive discussion of the BTE and derivation of these solutions can be found, for example, in ref. [3].

### 3.1.2. Boltzmann Transport Equation

The BTE essentially consists of writing the conservation of the number of the heat-carrying particles (i.e., electrons or phonons). The number of carriers follows a distribution function $f_k(r)$ which quantifies the number of carriers in a state defined by the wavevector $k$ in the neighborhood of the position $r$. The distribution at each location $f_k$ may evolve through i) diffusion, ii) external fields, and iii) scattering. In i), $k$-state carriers move in and out the neighborhood around $r$ as a result of their spatial velocity $v_k$ and the gradient of the distribution itself $\nabla f_k$. The diffusion contribution is then $\frac{\partial f_k}{\partial t} = -v_k \cdot \nabla f_k$. In ii), external fields can exert forces on the carriers (e.g., the Lorentz force for electrons, $F = -e(E_{\text{ext}} + [v_k \times \mu_k H_{\text{ext}}])$, due to external electric $E_{\text{ext}}$ and magnetic field $H_{\text{ext}}$). In general, a force $F$ induces a rate of change $\frac{\partial f_k}{\partial t_{\text{diff}}} = F \cdot \nabla f_k$. Finally, in iii), scattering processes cause a rate of change $\frac{\partial f_k}{\partial t_{\text{scatt}}}$, encompassing numerous interaction processes (e.g., for an electron, these include electron–electron, electron–phonon, electron–surface scattering). Approximations are often employed to reduce the complexity of such processes and ease their computational modeling. In particular, the relaxation time approximation is a common simplifying approach\[3,55\] which assumes that a slightly perturbed distribution $f$ is pulled back to its (local) equilibrium $f^0$ such that $\frac{\partial f_k}{\partial t_{\text{eq}}} = \frac{f^0 - f}{\tau}$, where $\tau = \tau(k, r, T)$ is the relaxation time.\[3,142\] Further assumptions about the involved scattering processes yield to a closed form expression for $\tau$.\[142\] However, these assumptions eventually limit the accuracy of this approach.\[143\] Overall, the conservation of the number of carriers in the neighborhood of $r$ can be written as:

$$\frac{\partial f_k}{\partial t} = \frac{\partial f_k}{\partial t_{\text{diff}}} + \frac{\partial f_k}{\partial t_{\text{field}}} + \frac{\partial f_k}{\partial t_{\text{scatt}}}$$

(15)

In the steady-state, $\frac{\partial f_k}{\partial t} = 0$.

The BTE expresses the dynamical state of the system of particles. The solution of the BTE for a system of phonons under the relaxation time approximation\[3,142\] leads to Cattaneo’s hyperbolic heat equation, and (under convenient approximations\[8\]) consequently, to Fourier heat conduction law. By solving the BTE for a system of electrons, instead, we can obtain the equations for electrical conduction and the electronic thermal flux equations expressed in the Onsager relations\[3,55\] such that carriers (electrons and phonons) play a role simultaneously, therefore, in principle, a system of equations with both carrier BTEs should be solved

$$\frac{\partial f_k}{\partial t} + v_k \cdot \nabla f_k + \mathbf{F} \cdot \nabla f_k = \frac{\partial f_k}{\partial t_{\text{scatt}}} + s'$$

(16)

$$\frac{\partial n_{k,s}}{\partial t} + v_{k,s} \cdot \nabla n_{k,s} = \frac{\partial n_{k,s}}{\partial t_{\text{scatt}}} + s''$$

(17)

where we denote $f_k$ as the electron distribution with $k$ wavevector and $n_{k,s}$ as the phonon distribution with wavevector $q$ and polarization $p$. Here, we have assumed that no external forces act on the phonons within the crystal. We denote $s'$ and $s''$ as source term rates of electrons and phonons, respectively.

The electron–phonon interaction will contribute to scattering terms both in $\frac{\partial f_k}{\partial t_{\text{scatt}}}$ and $\frac{\partial n_{k,s}}{\partial t_{\text{scatt}}}$. In steady-state, the terms $\frac{\partial f_k}{\partial t_{\text{scatt}}}$, $\frac{\partial n_{k,s}}{\partial t_{\text{scatt}}}$, $s'$, and $s''$ are equal to zero.

The macroscopic Fourier law, Equation (14), can be obtained from the BTE, by defining a thermal conductivity on the basis of transport of electrons or phonons (heat carriers).

### 3.1.3. The Thermal Conductivity

The thermal conductivity $\kappa_i$ related to the carrier $i$ ($i = e, \ell$ for electrons or phonons, respectively) can be obtained as a result of the BTE for carrier with an isotropic relaxation time approximation and averaging over carrier frequencies\[143\]

$$\kappa_i = \frac{\sqrt{C_i} \ell_i}{3}$$

(18)

where $C_i$ is the carrier heat capacity, $\ell_i$ is the average velocity of carriers, and $\ell_i$ is the mean free path. The thermal conductivity of a material $\kappa$ is given as the sum of the electron contribution $\kappa_e$ and the phonon contribution $\kappa_\ell$, $\kappa = \kappa_e + \kappa_\ell$.\[143,144\] The phonon contribution to the thermal conductivity is also referred to as the lattice thermal conductivity.

A main assumption is that electrons are the main heat carriers in metals, taking $\kappa = \kappa_e$, while phonons are the main heat carriers in non-metals (semiconductors and insulators).\[3\] This assumption is justified by realizing that the electronic thermal conductivity $\kappa_e$ in metals is much larger than the phonon thermal conductivity $\kappa_\ell$ (see, e.g., ref. [143]). Nevertheless phonons still have a non-negligible contribution in carrying heat in metals as we will see later in this section.

Contrary to electrons, for which transport processes take place at energies in the vicinity of the Fermi level, phonon transport processes involve phonons of energy $\hbar \omega$ in the whole spectral range described, at equilibrium, by the Bose–Einstein distribution at temperature $T$. To obtain the electronic thermal conductivity, one can use Equation (18) for electrons close to the Fermi level, obtaining $\kappa_e$, or directly solve the BTE, Equation (16).\[3\] Obtaining the phonon thermal conductivity $\kappa_\ell$ is more subtle as we need to analyze the contribution from phonons in a large spectral range.
Phonon Contribution to the Thermal Conductivity: Each phonon of energy $\hbar \omega$ is characterized by a spectral group velocity $v_\omega$ and mean free path $\ell_\omega$. The heat capacity $C_v$ denotes the contribution of phonons from the spectral interval $d\omega$ to the total heat capacity. The phonon thermal conductivity, following Equation (18), is then given by \cite{142,143,145}

$$\kappa_1 = \frac{1}{3} \sum_p [C_v v_{\alpha p} \ell_{\alpha p} d\omega]$$

(19)

where the variables are dependent on the phonon frequency $\omega$ and polarization $p$. We note also that the phonon thermal conductivity $\kappa_1$ can equivalently be written with components depending on the wavevector $q$ and polarization $p$, as linked by the phonon dispersion relation $\omega(q)$.

We now analyze, based on Equation (19), the main parameters contributing to the thermal conductivity and their role in the design and control of the phonon thermal conductivity $\kappa_1$.

The first parameter is the spectral heat capacity $C_v$ which depends on the phonon density of states. Its exact calculation is of numerical nature and can be obtained from the (material-dependent) lattice structure from first principles. However, the Debye and Einstein models are well known approximations for obtaining an analytical solution, especially well suited for acoustic and optical phonon branches, respectively.\cite{13,25}

The second parameter is the group velocity $v_{\alpha p}$ which can be obtained from the dispersion relation of phonons $\omega(q)$ by $v_{\alpha p} = \partial \omega/\partial q$. Considering typical phonon dispersion relationships (which can be experimentally obtained via, e.g., inelastic neutron scattering\cite{16,13,146} see Figure 4b for Si), it can be inferred that the group velocity of optical phonon modes is small, in contrast to the group velocity of acoustic phonons, suggesting that the optical phonon contribution to the thermal conductivity is negligible. However, optical phonons can decay in acoustic phonons contributing indirectly to the thermal conductivity.\cite{147}

The third parameter is the mean free path $\ell_{\alpha p}$ which depends on the different types of scattering involving phonons.\cite{13,143}

The mean free path is given by $\ell_{\alpha p} = \frac{\gamma_{\alpha p}}{\gamma_0}$ where $\gamma_0$ is the frequency-dependent phonon scattering rate. A common approach\cite{141,148} that scattering rates add up following the Matthiessen's rule $\gamma = \gamma_{e-e} + \gamma_{p-p} + \gamma_{i-i} + \gamma_{p-b} + \cdots$ where $\gamma_{e-e}$ refers to phonon–electron scattering, $\gamma_{p-p}$ refers to phonon–phonon scattering (via normal scattering processes at low temperatures and umklapp scattering processes at high temperatures\cite{149}), $\gamma_{i-i}$ to phonon-impurity scattering, and $\gamma_{p-b}$ to phonon-boundary scattering. Here, the scattering rates are frequency-dependent, but we dropped the $\omega$ subscript to simplify the notation. The scattering processes have distinct temperature dependence with different scattering processes dominating at different temperature ranges (see Figure 4c). It is possible to obtain closed form solutions for each of the scattering terms through approximations assuming an isotropic, Debye-like phonon spectrum consisting of one (averaged) phonon acoustic branch.\cite{142}

The combination of thermal conductivity measurements as function of temperature, $\kappa(T)$, and fitting procedures\cite{142} allows to retrieve information about the scattering mechanisms in different bulk materials.\cite{137}

In Figure 4c, we illustrate the $\kappa(T)$ dependence associated to the corresponding scattering mechanisms inferred from the temperature dependence. We note that, at a given temperature and for a given material and structure dimension, due to wavevector and frequency dispersion, phonons exhibit a range of mean free paths $\ell_{\alpha p}$ which can be larger or smaller than the hosting nanostructure.

Phonon Contribution to Thermal Conductivity Inside, at the Interface and in the Vicinity of Nanostructures: As the dimensions of a nanostructure becomes of the order of, or smaller than a phonon mean free path (ballistic-diffusive regime), the corresponding phonon thermal transport inside the nanostructure deviates from bulk values due to enhanced boundary scattering\cite{149–152} and/or a modified phonon density of states, caused by spatial confinement\cite{153–155} (which affects the heat capacity). As dimensions are shrunk, these effects result in a reduction of the phonon thermal conductivity of the nanostructure, when compared to bulk. Inside nanostructures smaller than a phonon mean free path, boundary scattering is typically the dominant scattering mechanism limiting transport.\cite{156} This situation was first analyzed by Casimir in 1938\cite{157} in his seminal work on heat transport in thin rods. In an analogy with photon transport, Casimir studied the case where phonon transport was considered as ballistic inside the rod and treated the rod surface as a blackbody where all the incident phonons are absorbed and re-emitted in all directions, an approximation which is equivalent to considering the rod surface as perfectly rough. Under these assumptions, for a cylindrical rod, the average phonon-surface mean free path is equal to the diameter of the rod\cite{141} (other geometries, such as, squared cross-section rods, can have different relation between the mean free path and the geometrical dimensions\cite{156}). This is often referred to as the Casimir limit. More recently, experimental studies have probed the Casimir limit in Si nanowires\cite{159} (and other geometries\cite{158}) also investigating the influence of the quality of the surface (rough/smooth) on the phonon transport process\cite{160} (whose impact on the heat transport process remains topic of debate\cite{152,158,161}).

In the case of an interface between two solid media, phonons can be transmitted or reflected, depending on the involved materials properties and the quality (rough/smooth) of the interface. It has been shown that, even if the interface between two different solid materials is perfectly smooth, a thermal boundary resistance, known as Kapitza resistance, develops at the interface due to a mismatch in phonon states in the two media\cite{156,161}. The Kapitza resistance can play an important role in the heat transport particularly as device sizes decrease below the carrier mean free path\cite{164,165} and at low temperatures.\cite{166}

In addition to size effects on phonon transport in processes occurring inside nanostructures, size effects also influence transport processes in the vicinity of small features. An interesting example of this situation is described in Chen\cite{130} where a sphere embedded in a substrate acts as a nanosource of heat. The heat generated in the sphere is carried away by phonons in the substrate, described by the Fourier law with the bulk thermal conductivity $\kappa$ of the material. As the sphere size (radius $R$) decreases below the (average) phonon mean free path $\ell$ in the substrate, less heat is transferred to the substrate when compared with the Fourier law prediction with bulk thermal conductivity and consequently less heat escapes the sphere, ultimately leading to a higher temperature in the sphere. This situation can be modelled by replacing the bulk
thermal conductivity $\kappa$ with a (size-dependent) effective thermal conductivity $\kappa_{\text{eff}}$. In Figure 4d, we show the calculated $\kappa_{\text{eff}}/\kappa$ as function of the particle size $R/L$, following Chen.[130]

Computation and Experimental Measurement of Phonon Contribution to Thermal Conductivity of Semiconductors and Dielectrics: Recent developments in computational capabilities and in first-principles computational packages allowed the study of thermal transport from first-principles in semiconductors and the comparison between theoretical predictions and experimental measurements of the thermal conductivity. For example, first-principles simulations in semiconductors by Brodo et al.[167] for Si and Ge (see Figure 5a), Esfarjani et al.[139] for Si and Lindsay et al.[168] for BAs obtain a calculated phonon thermal conductivity in good agreement with experiments. In particular, first-principles calculations by Esfarjani et al.[139] in Si specifically address the contribution of different phonon modes (i.e., longitudinal acoustic, transverse acoustic, longitudinal optical and transverse optical) and mean free paths to the thermal conductivity of Si. Esfarjani et al. obtained that the thermal conductivity of Si at room temperature includes phonons with mean free paths spanning over five orders of magnitude (from 1 nm to 100 μm). Additionally, it was calculated that about half of the thermal conductivity is due to phonons with mean free paths larger than 1 μm.[139]

Although these simulations provide valuable insights into transport mechanisms, the experimental validation of such results is challenging since discerning the different phononic contributions depending on different mean free paths is not straightforward. Recent experimental studies[134,174] assume non-diffusive phonon transport in Si[169,170] to infer the contribution to the thermal conductivity from phonons with various mean free paths. Further experimental efforts[169,170,173] take advantage of the Time-Domain Thermoreflectance (TDTR)[176] (or alternatively Frequency-Domain Thermoreflectance, FDTR[177]) technique to measure the thermal conductivity of materials. In particular, TDTR has been shown to be a powerful technique to determine the thermal conductivity for a great range of materials[178] by monitoring the temperature induced changes in the intensity of an optical beam reflected at the sample surface. Figure 5b shows a schematic of the strategy followed in refs. [169,170] where a sub-micron size heat source generates a range of non-equilibrium phonons that decay in the proximity of the source, establishing a local equilibrium temperature. If the source is smaller than a phonon mean free path $l_{\text{ph}}$ (Figure 5b(ii)), a phonon of mean free path $l_{\text{ph}}$ will not contribute to the local equilibrium and therefore the thermal conductivity measured by TDTR will be smaller than the bulk thermal conductivity $\kappa$ (e.g., the recurring example of the nanosphere of smaller dimensions than the mean free path embedded in the substrate as in Chen[130]). In Figure 5c adapted from[169], it is shown how the obtained thermal conductivity seems to indicate an onset to non-diffusive transport. From these measurements it is possible to reconstruct the cumulative thermal conductivity distribution with the mean free path, as exemplified, for example, in Figure 5d from[139], allowing the comparison to first principles simulation results.[139,167]

Computations and Experimental Measurement of Phonon Contribution to Thermal Conductivity in Metals: In metals, it is generally assumed that the thermal conductivity is dominated by the electronic contribution $\kappa_e$. To study the validity of this assumption, recent first-principles computations calculated both the electronic and phonon thermal conductivities in bulk Al, Ag, and Au, by Jain et al.[175] (see Figure 5e and f) and in bulk Cu, Ag, Au, Al, Pt, and Ni, for the phonon thermal conductivity, by Wang et al.[179]. In metallic films and nanowires of Au, Ag, Cu, Al, Ni, Pt and W with dimensions in the 25 to 500 nm range, Stojanovic et al.[172] conclude that phonon thermal conductivity $\kappa_p$ becomes more important as the size is decreased. Stojanovic et al.[172] (Figure 5g) further obtain that less than 10% of the overall thermal conductivity $\kappa$ is given by the phonon contribution $\kappa_p$. In Ag and Au (higher contribution $\kappa_p/\kappa$ has been obtained for other metals, with 10% being a typical contribution in several metals[172,180]).

Measuring $\kappa_p$ in metals is experimentally challenging[181,182] and therefore its calculation often relies on its estimation by subtracting the electronic contribution to the thermal conductivity $\kappa_e$ obtained with the Wiedemann-Franz (WF) law, from the experimentally measured thermal conductivity $\kappa$. The WF law states that the thermal conductivity of a metal, where the heat transport is dominated by electrons, is simply proportional to its electrical conductivity, with a material dependent proportionality constant known as the Lorenz number.[25,183] The assumptions underneath the WF law is that heat is predominantly transported by electrons and scattering is mostly elastic.[25] This is largely valid for bulk metals. However, some controversy exists regarding its validity at the nanoscale.[172] as both enhancements[184] and reductions[185] of the Lorenz number have been reported. We illustrate a recent investigation of the WF law by atomic point contact spectroscopy.[173,186,187] In Figure 5h, Cui et al.[173] report independent measurements of thermal and electric transport in a gold single-atom junction formed with a modified scanning probe, confirming the validity of the WF law, if the assumptions above are fulfilled. Another experimental strategy to study thermal transport in metals relies on the effect on optical properties measured by thermoreflectance or transmission studies and is of special importance in ultrafast laser spectroscopy studies that we cover in Section 4.

3.2. Wave-Like Phonon Transport and Phononic Crystals

In Section 3.1 and 3.1.3, we have described heat transport by electrons and phonons. The exposition presented considered a particle representation of the heat carriers.

3.2.1. Transport as Wave

As quantum mechanical objects, electrons and phonons have a wave-particle dual nature.[18] In the wave representation, electrons and phonons have a coherence property, being coherent if the their associated wave preserves its phase. However wave-like electrons and phonons can dephase during inelastic scattering events (e.g., electron–phonon scattering). In contrast, in elastic scattering, for example, specular boundary scattering (reflections), the wave-like electrons or phonons retain their phase. The propagation length in which the wave-like electron or phonon keeps its phase is defined as coherence length.
In Section 3.1.3, the main contributions to phonon thermal conductivity were outlined without considering wave-like phonon effects. Wave-like effects such as reflections and transmissions at interfaces can induce phonon coherent interference. Wave interference effects, if controllable, can create fundamentally new strategies for manipulating the...
heat flow. We now analyze how new approaches enable customized heat transport when the transport is carried by wave-like phonons.

We have introduced the link between phonons and lattice waves in Section 1. The link comes from the decomposition of lattice waves into lattice modes. Now we turn the attention to the propagation of lattice waves and corresponding phonons.

### 3.2.2. Elastodynamics Equation for Phonon Propagation as Wave

The computation of lattice waves propagation lattice waves in solids is enormously simplified by considering the solid material as a continuous elastic medium instead of an ensemble of individual atoms, as done in lattice dynamics\(^\text{[2,3,154]}\). Both lattice dynamics equations and elastic continuum equations are equivalent in the limit of long phonon wavelengths \(\lambda\) with respect to the atomic lattice constant \(a\), \(\lambda \gg \pi a\). This equivalence allows the use of classical theory of elasticity to describe phonon propagation as elastic waves. The phonon dynamics is thus described by the Navier elastodynamics equation,\(^\text{[189]}\) that for an heterogeneous isotropic medium can be written as

\[
\rho \frac{\partial^2 \mathbf{u}(r,t)}{\partial t^2} = \nabla \left[ (\lambda + 2\mu) \nabla \cdot \mathbf{u}(r,t) \right] - \nabla \times \left[ \mu \nabla \times \mathbf{u}(r,t) \right]
\]

(20)

where \(\rho\) is the (position-dependent) material density, \(\lambda\) and \(\mu\) are the Lamé coefficients, \(\mathbf{u}\) is the displacement vector and \(r\) is the position vector. The density \(\rho\) and the coefficients \(\lambda\) and \(\mu\) are elastic constants of the material.

The elastic wave propagation is more generally described by a tensor equation capable of including potential anisotropies of the lattice: considering\(^\text{[189]}\) \(i = 1, 2, 3\) for different Cartesian directions, we can write

\[
\rho \frac{\partial^2 \mathbf{u}_i(r,t)}{\partial t^2} = \sum_{jkl} \frac{\partial}{\partial x_j} \left( C_{ijkl} \frac{\partial u_l}{\partial x_k} \right)
\]

(21)

where \(C_{ijkl}\) represents the stiffness tensor (in an isotropic solid it can be constructed from the materials constants \(\rho\), \(\lambda\) and \(\mu\)). Equation (20) can, in effect, be derived from Equation (21). Detailed derivation and discussion regarding properties of equations 20 and 21 can be found in refs. \(^\text{[189,190]}\). Extensive compilations of materials elastic constants can be found in ref. \(^\text{[191]}\), and in ref. \(^\text{[25]}\) for some cubic crystals.

The spectrum of allowed phonon modes, within the elastic approximation, can be obtained by calculating the eigenfrequency spectrum for the elastodynamic equation, depending on the material elastic properties and geometry of the structure. For spheres (both homogeneous and core–shell) and rods, analytic expressions for the eigenfrequencies can be derived.\(^\text{[51,192]}\) For other shapes, the vibrational modes must be calculated numerically, using for example the finite element method (FEM). A good agreement between transient-absorption spectroscopy measurements and FEM results has been shown for example in Au–Ag nanoboxes and nanocages of dimensions \(\approx 35–90\) nm with aspect ratios of \(\approx 8–9\) using bulk elastic constants.\(^\text{[195]}\) The use of bulk elastic constants was shown to be valid down to nm-sized objects, allowing to predict the vibrational frequencies, 1.1–2.6 THz, of spherical particles for Pt with 1.3–3 nm diameter (estimated 75–950 atoms).\(^\text{[194]}\)

### 3.2.3. Phononic Crystals

We now analyze how to influence phonon propagation, leveraging on its wave-like description. The basic idea is to design a structure where transport is strongly influenced by wave interference, in analogy with photonic crystals.\(^\text{[195]}\)

In fact, by constructing a periodic structure that supports coherent phonons employing materials of different elastic properties (\(\rho\), \(\lambda\), and \(\mu\) in Equation (20)), a propagating phonon wave can be reflected at the interfaces and interfere constructively or destructively. The result is a phononic bandstructure possibly featuring phonon bandgaps, forbidding the propagation of specific phonon modes, that is, a phononic crystal (PnC), see Figure 6a.\(^\text{[196,197]}\)

Under the assumption of coherent thermal phonon transport, by choosing material and geometry, a PnC could allow the creation of a phonon bandgap at thermal frequencies,\(^\text{[19,198]}\) a thermal bandgap, where phonons cannot propagate (as a direct result of the interference effects between phonon modes) causing the thermal conduction to be carried by phonons of different frequency ranges than in bulk.\(^\text{[19,198,199]}\) A typical PnC is, for instance, a Si membrane patterned with air holes (cylinders) as fabricated, for example, in Maire et al.\(^\text{[21]}\) and whose operation is experimentally demonstrated at low temperatures (<10 K). Considering such structure as an example, without loss of generality, to observe the effect of wave interference, the features of the PnC should be smaller than the phonon mean free path (in fact, than the phonon coherence length)\(^\text{[180,200,201]}\) in Si and the Si-air interfaces should be smooth with a roughness smaller than the phonon wavelength, allowing specular reflections at the interface.\(^\text{[202,203]}\) For example, in bulk Si, Esfarjani et al.\(^\text{[139]}\) predicted that the phonons contributing to the thermal conductivity have wavelengths between 1–30 nm at room temperature, implying a required PnC interface roughness in the sub-nm scale. Another requirement is the absence of inelastic scattering during propagation. Absence of scattering is a good approximation for photons and a reasonable approximation for mechanical phonons (e.g., kHz to GHz range).\(^\text{[204]}\) For thermal phonons (in the THz range), due to phonon–phonon scattering events which dominate at high temperature, the requirement is fulfilled only at low temperatures, or in nanostructures with feature sizes much smaller than the mean free path. Figure 6a illustrates the concept of a PnC as proposed by Maldovan and realized by Zen et al.\(^\text{[200]}\) (Figure 6a(ii) and Figure 6a(iii)). In particular, Figure 6a(ii) shows the calculated phononic bandstructure for a fabricated SiN PnC structure (Figure 6a(ii)) in Zen et al. with the presence of a phononic bandgap around 3 GHz.

The control of heat transport through the manipulation of phonons as coherent waves was experimentally observed in 1D and 2D PnCs. In 1D, Luckyanov et al.\(^\text{[216]}\) used a metal-organic vapor deposited lattice-matched 1D superlattice (SL)
of GaAs/AlAs with 12 nm thickness/layer obtaining a linear increase of the measured thermal conductivity with the SL thickness in the temperature range 30 – 150 K, consistent with a coherent phonon heat transport; and Ravichandran et al.[206] used epitaxially-grown perovskite superlattice structures of SrTiO$_3$/CaTiO$_3$ and SrTiO$_3$/BaTiO$_3$ and varied the superlattice period thicknesses from 57 to 293 nm, obtaining a minimum of the thermal conductivity as function of the period thickness.

Figure 6. a) Phononic crystal (PnC). i) Geometry of a 2D PnC (from ref.[205]); ii) calculation of the phonon dispersion for same 2D PnC (Lamé coefficients $\mu = 101.63$ GPa and $\lambda = 3.72$ GPa) by FEM under Floquet periodic condition (see ref.[20]); iii) SEM image of a fabricated 2D PnC of circular holes of air with radius $r$ in a square unit cell of SiN with side $a = 970$ nm, ratio r/a = 0.47. Reproduced with permission. Copyright 2014, Springer Nature. b) 1D PnC.[206] i) STEM-EELS image of a (SrTiO$_3$/BaTiO$_3$)$_x$ SL. Reproduced with permission. Copyright 2013, Springer Nature; ii) Measured thermal conductivity values for SLs versus interface density at different temperatures. Reproduced with permission. Copyright 2013, Springer Nature. c) Reported thermal conductivity in porous Si thin films vs limiting dimension, replotted from ref. [207] for experimental data reported in the literature.[208–214] (black line representing theoretical cumulative thermal conductivity of Si[207]). Inset illustrates the limiting dimension (Reproduced with permission. Copyright 2015, American Physical Society). d) Coherent phonon heat transport in 1D and 2D Si PnCs, i1) (and ii1) 1D (and 2D) PnC with ordered and disordered hole pattern and i2) (and ii2) Thermal conductivity versus disorder parameter for 1D (and 2D) Si PnCs at $T = 4$ K and $T = 300$ K (from supplementary materials of ref. [21]).
both at low and room temperature (Figure 6b), a theoretically predicted\(^{225}\) indication of the crossover from incoherent to coherent transport. Previous experiments had already reported reduced conductivities in 2D\(^{208,210–215,218}\) for different PnC structures with different limiting dimensions, as shown in Figure 6c.\(^{220}\) However some theoretical works suggested that the observed thermal conductivity reduction in Si PnCs is not the result of phonon interference but it is rather due either to surface roughness, strong surface scattering at room temperature\(^{219}\) or phonon–phonon interactions for temperatures higher than 130 K.\(^{204}\) Adding to the discussion, a recent work by Maire et al.\(^{21}\) reports coherent phonon interference effects in both 1D and 2D PnCs of Si at 4 K indicating wave effects to account exclusively for the thermal conductivity reduction at low temperatures (see Figure 6d).

In all these studies, phonon coherence is a key enabler for wave-like interference. The phonon coherence length thus determines whether we should model heat transport starting from the phonon wave representation or treat phonons as particles. However, in contrast to photon coherence length, there is no widely used definition of phonon coherence length.\(^{222}\) A definition drawn by analogy with coherence theory for black-body radiation was proposed in Chen.\(^{206}\) Chen definition of the coherence length depends on the spectral width of the source, the medium through which the wave propagates, and the bandwidth of the detector. For heat conduction by phonons, both the heat source (thermally excited phonons) and the detector (i.e., temperature sensor) cover a wide spectrum of the phonons and the coherence length is thus expected to be short, for example, Chen calculated a coherence length in the order of 1-2 nm at room temperature for GaAs.\(^{206}\) More recently, Latour et al.\(^{200}\) proposed a microscopic theory of the phonon spatial coherence length based on correlation theory. In another work, Latour et al.\(^{221}\) used correlation theory to include spatial and temporal coherence, analyzing transport in a SL, defining coherent and incoherent transport regimes with relation to the phonon mean free path and the spatial coherence length.

### 3.2.4. Summary of Transport Regimes

In Sections 3.1 and 3.2, we have described the modeling strategies for heat transport in particle or wave representation, encompassing different transport regimes. In practice, the comparison between the characteristic dimension of the system \(d\) and the (material-dependent and frequency-dependent) mean free path \(l_\omega\) and coherence length \(L_\omega\) determines which equations we should employ when we start modeling heat transport. We summarize this information in Table 1.

A key element to control thermal propagation is the ability to excite coherent phonons. So far, in this review, we have focused on analyzing the transport mechanisms and phonon manipulation strategies, regardless of how phonons were excited. A common procedure to excite phonons is carried out by mechanically coupling the phononic crystal with a laser heated metallic layer (heat source).\(^{21,205,206,216}\) Although phonons can be generated from the heat source,\(^{205}\) thermal phonons, as a result of the scattering processes required to reach equilibrium, are typically incoherent and controlling their phase relationship poses serious challenges.\(^{222}\) In principle, non-equilibrium phonons can also be transferred across the interface between the heated and surrounding medium and this mechanism is still a subject of investigation.\(^{210,222}\) These phonon excitation processes provide a potential ground to bridge plasmonics and phononics, as described in Section 4, where the focus will be on phonon generation in plasmonic (metallic) nanostructures. Other materials, (e.g., semiconductors) can support different mechanisms of phonon excitation (e.g., electrostriction, piezoelectricity) that will not be explored in this review. The interested reader is referred, for example, to refs. \(^{72,223}\) for further information.

### 4. Intersection between Plasmonics and Phononics

As seen in Section 2, the absorption of electromagnetic radiation in plasmonic materials is microscopically described by electronic transitions. Upon interaction between an EM field and a plasmonic structure, the EM energy is transferred to the metal generating a non-equilibrium electronic population. This non-equilibrium population will relax through electron–electron, electron–phonon and electron–surface interactions. Ultimately, the (material-dependent) electron–phonon interaction eventually sets the total amount of energy transferred to the lattice resulting in thermal and vibrational effects. The study of these mechanisms and their characteristic timescales has become possible with the development of ultrafast laser spectroscopy and pump-probe techniques, utilizing ultrashort laser pulses of fs duration.\(^{96,224}\)

#### 4.1. Pump-Probe and Two-Temperature Model

##### 4.1.1. Pump-Probe Experimental Principle

In a typical pump-probe experiment, an ultrashort laser pulse (the pump) produces a non-equilibrium (athermal) electron

---

**Table 1. Models of heat transport.**

| Representation | Transport regime | Size condition | Equation |
|---------------|-----------------|----------------|---------|
| Diffusive     | \(d \gg l_\omega\) | BTE (Fourier law, Equation (14)) |
| Particle      | Ballistic-Diffusive | \(d = l_\omega\) | BTE (Equation (15)) |
|              | Ballistic       | \(d \ll l_\omega\) | BTE (radiative transfer) |
|              | Coherent        | \(d \ll L_\omega\) | Lattice dynamics (Newton’s second law) |
| Wave          |                 | Elastodynamics (continuum approximation in long wavelength limit, Equation (20)) |

\(d\) refers to the characteristic size of the system under study, \(l_\omega\) refers to the mean free path at frequency \(\omega\) and \(L_\omega\) to the coherence length at frequency \(\omega\).
population. An equilibrium (thermal) electron population with equilibrium temperature $T_e$ is reached through electron–electron scattering in the $\approx 10–100$ fs timescale. Both athermal and thermal electrons exchange energy with the lattice, which is at a lower equilibrium temperature $T_L$, by emitting phonons. The combination of these microscopic processes following the initial pump pulse can modify the electric permittivity of the structure and thus of its optical response. The time variation of the optical response can be monitored by measuring, for example, the change in reflection $\Delta R / R$ or transmission $\Delta T / T$ using a lower intensity probe pulse that illuminates the sample at different time delays with respect to the initial probe pulse.[225]

### 4.1.2. Two-Temperature Model

The dynamics of the electron and phonon populations is described by the corresponding BTE (Equation (16) or (17)) with an illumination-dependent electronic source term ($\epsilon^0$ in Equation (16)). The model is simplified under the assumption of equilibrium electron and lattice sub-systems where the transfer of energy from the electrons to the lattice is expressed in the well-known Two-Temperature Model (TTM). First proposed by Anisimov et al.[226] the TTM consists of a system of equations for the electron and lattice temperature evolution in time where an additional heat diffusion equation can be added to include the heat transferred from the lattice to an external system (e.g., the surrounding medium):

$$C_e(T_e) \frac{dT_e}{dt} = V \cdot (\kappa_e(T_e, T_i) \nabla T_e) - G(T_e)(T_e - T_i) + S(r,t)$$ (22)

$$C_L(T_L) \frac{dT_L}{dt} = V \cdot (\kappa_L(T_L) \nabla T_L) + G(T_e)(T_e - T_L)$$ (23)

where $C_e$ and $C_L$ are the electron and lattice heat capacities, $\kappa_e$ and $\kappa_L$ are the thermal conductivities due to electrons and phonons, $G(T_e)$ is the electron–phonon coupling, dependent on the electronic temperature $T_e$. $T_L$ is the lattice temperature and $S(r,t)$ describes the power density deposited by the laser pulse (e.g., $q_{laser}$ Equation (8)). Allen[229] showed that the TTM equations (22) and (23) can be obtained from the BTE system of equations for electrons and phonons (see Equations (16) and (17)) providing a microscopic theoretical description of the energy transfer process.

### 4.1.3. Parameters That “Control” Energy Transfer in the TTM

The rate at which the energy is transferred from the electron to the lattice sub-system is controlled by the electron–phonon coupling $G$.[228–230] In Allen[229] $G$ is obtained by computing the probability of scattering between electron and phonon states, applying the Fermi Golden Rule, thus making $G$ depend on the Eliashberg coupling function $\alpha^2 F(\omega)$ (which has been introduced in the electron–phonon scattering rate in Equation (2)).

The parameters $C_e$, $C_L$, and $G$ are temperature dependent, as explicitly written in Equations (22) and (23). However, by considering a temperature-independent $G$ and linear temperature dependence for $C_e$ and $C_L$, ref. [226] obtained a satisfactory fit of experimental data. With knowledge of the parameters $C_e$, $C_L$ and $G$, the TTM system (Equations (22) and (23)) can be solved numerically for the time evolution of equilibrium temperatures of both sub-systems $T_e$ and $T_L$[226] for bulk and thin film gold (see Figure 7a). A compilation of experimentally inferred values for these parameters in Au, Co, Cr, Cu, Mo, Ni, Pt, and Ru can be found in ref. [226]. The same work[226] also gives a comprehensive list of experimentally determined electron–phonon coupling $G$ for Au with $G$ in the range $1–4 \times 10^{16}$ W m$^{-3}$ K$^{-1}$. Additionally, comprehensive lists of the experimentally determined electron–phonon coupling constants are present in refs. [226,230] revealing materials with weak electron–phonon coupling (e.g., Au and Ag with $G = 3 \times 10^{16}$ W m$^{-3}$ K$^{-1}$) compared to other material of stronger electron–phonon coupling (typically in the range $1–10 \times 10^{17}$ W m$^{-3}$ K$^{-1}$, as for example Ni with $G = 8 \times 10^{17}$ W m$^{-3}$ K$^{-1}$[231]).

The parameters $C_e$, $C_L$, and $G$ ultimately depend on the electronic bandstructure and phonon dispersion which can be obtained from first principles simulations. For example, Lin et al.[230] provided $C_e$, $C_L$, and $G$ as a function of temperature for Al, Ag, Cu, Au, Ni, Pt, W, and Ti-based on the first-principles simulation of their respective bandstructures. The values obtained in[230] were compared against previous works,[226] showing considerable deviations. More recently, Brown et al.[95] have presented parameter-free first-principles calculations of plasmonic metals (Ag, Au, Cu) including interband transitions obtaining more refined values for the parameters $C_e$, $C_L$, and $G$ when compared to ref. [230].

### 4.1.4. Experimental Pump-Probe Studies and TTM Analysis

In Figure 7b[226] we report the comparison between a pump-probe reflectance experiment obtained for thin films of Au with different thicknesses, showing a good correspondence between TTM and experimental data. The validity of the TTM assumes both the electronic and phononic sub-systems to be at equilibrium. The more general case where both sub-systems are in non-equilibrium can be treated employing the full BTE system of equations.[229] In particular, fully non-equilibrium models consider the transport of energy from electrons to particular phonon modes.[232] Models based directly on the BTE have also been used with success to quantitatively match the experimentally measured $\Delta T / T$ data in 23 nm Ag and $\Delta R / R$ data in 20 nm Au films.[233] Pump-probe experiments have also been conducted in metallic nanoparticles,[227] see Figure 7c(i) where optical information is more easily extracted considering a temperature-independent $G$ and linear temperature dependence for $C_e$ and $C_L$, ref. [226] obtained a satisfactory fit of experimental data. With knowledge of the parameters $C_e$, $C_L$, and $G$, the TTM system (Equations (22) and (23)) can be solved numerically for the time evolution of equilibrium temperatures of both sub-systems $T_e$ and $T_L$[226] for bulk and thin film gold (see Figure 7a). A compilation of experimentally inferred values for these parameters in Au, Co, Cr, Cu, Mo, Ni, Pt, and Ru can be found in ref. [226]. The same work[226] also gives a comprehensive list of experimentally determined electron–phonon coupling $G$ for Au with $G$ in the range $1–4 \times 10^{16}$ W m$^{-3}$ K$^{-1}$. Additionally, comprehensive lists of the experimentally determined electron–phonon coupling constants are present in refs. [226,230] revealing materials with weak electron–phonon coupling (e.g., Au and Ag with $G = 3 \times 10^{16}$ W m$^{-3}$ K$^{-1}$) when compared to other material of stronger electron–phonon coupling (typically in the range $1–10 \times 10^{17}$ W m$^{-3}$ K$^{-1}$, as for example Ni with $G = 8 \times 10^{17}$ W m$^{-3}$ K$^{-1}$[231]).

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### 4.1.4. Experimental Pump-Probe Studies and TTM Analysis

In Figure 7b[226] we report the comparison between a pump-probe reflectance experiment obtained for thin films of Au with different thicknesses, showing a good correspondence between TTM and experimental data. The validity of the TTM assumes both the electronic and phononic sub-systems to be at equilibrium. The more general case where both sub-systems are in non-equilibrium can be treated employing the full BTE system of equations.[229] In particular, fully non-equilibrium models consider the transport of energy from electrons to particular phonon modes.[232] Models based directly on the BTE have also been used with success to quantitatively match the experimentally measured $\Delta T / T$ data in 23 nm Ag and $\Delta R / R$ data in 20 nm Au films.[233] Pump-probe experiments have also been conducted in metallic nanoparticles,[227] see Figure 7c(i) where optical information is more easily extracted considering a temperature-independent $G$ and linear temperature dependence for $C_e$ and $C_L$, ref. [226] obtained a satisfactory fit of experimental data. With knowledge of the parameters $C_e$, $C_L$, and $G$, the TTM system (Equations (22) and (23)) can be solved numerically for the time evolution of equilibrium temperatures of both sub-systems $T_e$ and $T_L$[226] for bulk and thin film gold (see Figure 7a). A compilation of experimentally inferred values for these parameters in Au, Co, Cr, Cu, Mo, Ni, Pt, and Ru can be found in ref. [226]. The same work[226] also gives a comprehensive list of experimentally determined electron–phonon coupling $G$ for Au with $G$ in the range $1–4 \times 10^{16}$ W m$^{-3}$ K$^{-1}$. Additionally, comprehensive lists of the experimentally determined electron–phonon coupling constants are present in refs. [226,230] revealing materials with weak electron–phonon coupling (e.g., Au and Ag with $G = 3 \times 10^{16}$ W m$^{-3}$ K$^{-1}$) when compared to other material of stronger electron–phonon coupling (typically in the range $1–10 \times 10^{17}$ W m$^{-3}$ K$^{-1}$, as for example Ni with $G = 8 \times 10^{17}$ W m$^{-3}$ K$^{-1}$[231]).

The parameters $C_e$, $C_L$, and $G$ ultimately depend on the electronic bandstructure and phonon dispersion which can be obtained from first principles simulations. For example, Lin et al.[230] provided $C_e$, $C_L$, and $G$ as a function of temperature for Al, Ag, Cu, Au, Ni, Pt, W, and Ti-based on the first-principles simulation of their respective bandstructures. The values obtained in[230] were compared against previous works,[226] showing considerable deviations. More recently, Brown et al.[95] have presented parameter-free first-principles calculations of plasmonic metals (Ag, Au, Cu) including interband transitions obtaining more refined values for the parameters $C_e$, $C_L$, and $G$ when compared to ref. [230].
4.2. Mechanisms for Excitation of Coherent Phonons Using Light

The electron–phonon interaction dynamics eventually generates a spectrum of propagating phonons in the nanostructure. As previously mentioned (Section 3.2), the description of phonon propagation can be simplified considering the elastic approximation. In fact, it is the coherent stress induced by their propagation that allows phonons to be treated as lattice waves.

4.2.1. Elastodynamics Equation with Force Term

In this framework, the effect of light can be accommodated by considering an external force term in the elastodynamics equation, Equation (21). We thus modify the elastic tensor equation

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \sum_{ijkl} \frac{\partial}{\partial x_i} \left( C_{ijkl} \frac{\partial \mathbf{u}}{\partial x_j} \right) + f_{\text{imp},i} \tag{24}$$

where $C_{ijkl}$ represents the stiffness tensor and $f_{\text{imp},i}$ an impulsive force term (per unit volume) originated by thermal processes.

The impulsive force term can considered as the result of a photoinduced stress $\sigma(x,t)$. For instance, we can write

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = \frac{\partial^2 \mathbf{u}}{\partial z^2} + \rho \frac{1}{\rho} \frac{\partial \sigma_{zz}(z,t)}{\partial z} \tag{25}$$

where $\mu$ is the second Lamé coefficient (shear modulus), $\rho$ is the material density and $\sigma_{zz}$ is a tensor component of the photoinduced stress.

Following a mathematical procedure described in ref. [223] it is possible to compute the spectrum of emitted phonons (treated as elastic waves) for any induced stress $\sigma$. By treating phonons as elastic waves, this approach is implicitly suited for the study of generation of coherent phonons.

The first observation of photoinduced coherent phonon generation was made by Thomsen et al. first in semiconductors and later in metals. Thomsen et al. used a picosecond pump-probe experiment where oscillations in the transmission and reflection signal were attributed to the generation and propagation of coherent phonons as a consequence of the
photoinduced stress simultaneously due to electrons\(^{(75)}\) and phonons\(^{(93,237)}\)

\[
\sigma = \sigma_e + \sigma_p = -\sum_k \delta f_k(t) E_k \gamma_k - \sum_q \delta n_q(t) \hbar \omega_q \gamma_q^p
\]  

(26)

where \(\delta f_k(t) = f_k(t) - f_0^p\) and \(\delta n_q(t) = n_q^e(t) - n_q^{p0}\) refer to photoinduced time-dependent changes with respect to the initial electron and phonon distributions \(f_0^p\) and \(n_0^p\). \(E_k\) and \(\hbar \omega_q\) are the energies of electron and phonon of wavevector \(k\), and \(\gamma_q^e\) are the Grüneisen parameters for electron and phonon, respectively\(^{(235,237)}\). The distributions \(f_k(t)\) and \(n_q(t)\) can be obtained from the BTE system of equations 16 and 17. A simplified equation, Equation (26), considers each of the sub-systems in equilibrium with respective temperatures \(T_e\) and \(T_L\) and constant Grüneisen parameters (not varying with \(k\) or \(q\)) so that

\[
\sigma = \sigma_e + \sigma_p = -\gamma^e C_e \delta T_e(t) - \gamma^p C_p \delta T_L(t)
\]  

(27)

where \(C_e\) and \(C_p\) are the heat capacities of electron and lattice and \(\delta T_e(t)\) and \(\delta T_L(t)\) are the temperature increase in the electron and lattice sub-systems, respectively. The temperatures \(T_e\) and \(T_L\) can be obtained from the TTM system of equations (22) and (23). The spatio-temporal characteristics of the photoinduced stress is dependent upon the electron and phonon interaction dynamics already introduced in Section 4.1.

Regarding the involved time scales, the electron contribution to the photoinduced stress is dominant on a very short timescale (typically \(\approx 1\) ps)\(^{(233,238,239)}\) while the lattice contribution is dominant at a longer timescale (typically \(\approx 10\) ps)\(^{(239)}\).

Regarding the length scale, two main situations can be identified: in metals where the electron–phonon coupling is strong (e.g., in Ni), the lattice is heated very fast and it is a good approximation to assume hot-electrons do not leave the pump light absorption area (as the characteristic distance over which they deposit their energy into the lattice\(^{(237)}\) can be approximated by \(L = \sqrt{\kappa / G}\) where \(G\) is the electron–phonon coupling constant is of the order of the optical skin depth); in metals where the electron–phonon coupling is weak, instead (e.g., noble metals) hot-electron diffusion is extended over a distance much larger than the optical pump, which can be as large as \(L = 100\) nm in Au\(^{(237,240)}\) and therefore the spatial profile of the emitted phonons depends on the profile of the hot-electron energy release.

Following the relaxation of excited electrons, the emitted phonons (which have no phase relation between each other) contribute to lattice heating via phonon–phonon interactions and, due to the lattice anharmonicity, lead to a rapid lattice thermal expansion and mechanical structural changes. The stress associated with the expansion is \(\sigma = -3B\beta \Delta T\) with bulk coefficient \(B\) and linear thermal expansion coefficient \(\beta\) thus being referred to as thermoelastic stress. This stress contributes to the excitation of phonon modes (via, e.g., in 1D, Equation (25)) treatable as lattice waves. The lowest frequency radial mode of a nanostructure (breathing mode) and its harmonics, are commonly excited via this procedure\(^{(224)}\). The induced cyclical structural expansions and contractions cause the appearance of a small periodic change in the volume of the structure and, consequently, a periodic change of the dielectric constant that can be detected as a transmission variation with a probe pulse (see, e.g., Figure 9a). The generated acoustic phonons, are typically in the GHz range\(^{(245)}\) (and can thus be referred to as mechanical phonons) with coherent phonon generation demonstrated for frequencies up to the THz range in Juve et al.\(^{(194)}\). However, while the elastodynamics equation remains valid for nm-scale objects (Section 3, refs. [188,193]), for sub-nm structures smaller than the hot-electron mean free path, this approach has been shown to break down and the suppression of phonon waves has been observed\(^{(228)}\).

4.2.2. Elastodynamics with Thermoplasmonic Heating of Sphere

The material and the geometry of a nanostructure will critically influence the phonons that can be supported (and emitted). We illustrate this concept with the recurrent example of a Au sphere with \(R = 40\) nm immersed in water. In the discussion of Section 2.2 we found that, for this typical example in thermoplasmonics, the steady-state temperature rise, under \(2.5\) mW \(\mu\)m\(^{-2}\), was \(\Delta T_0 = 157\) K (see Figure 3b). We now consider the phonon waves generated due to lattice thermal expansion (via thermoelastic stress). To exemplify this situation, we consider water as an elastic medium where elastic waves can propagate with wavevector \(k\) (in fact water is a fluid and does not support such elastic waves, but pressure waves which bear similarities to the longitudinal lattice waves). The elastodynamics equation, Equation (24), in case of an isotropic medium, takes the form\(^{(189)}\)

\[
\rho \frac{\partial^2 u}{\partial t^2} = \nabla[(\lambda + 2\mu)(\nabla \cdot u)] - [\nabla \times \mu[\nabla \times u] - 3(\lambda + 2\mu)\beta \nabla T
\]  

(28)

and for a spherical geometry

\[
\rho \frac{d^2 u}{d\tau^2} = (\lambda + 2\mu) \left[ \frac{d^2 u}{dr^2} + \frac{2 du}{dr} - \frac{2u}{r^2} \right] - 3(\lambda + 2\mu)\beta \frac{dT}{dr}
\]  

(29)

With boundary conditions for continuity of the displacement and stress at the interface \(r = R\) and limit conditions of finite solution at origin (no displacement at \(r = 0\)) and a propagating wave in the surrounding medium \(u_i(t) \propto \exp(ikr)/r\), where \(k\) is the wavevector of the propagating wave, the solution takes the form of a damped oscillator. At the interface, \(r = R, u(R,\phi) = A_R \exp(i\omega t + i\phi) = A_R \exp(-\gamma R)\cos(\omega t + \phi)\) with amplitude \(A_R = R\beta \Delta T\) where \(\Delta T\) is a temperature increase, which here is considered as the steady-state temperature increase (for simplicity, we disregard ultrafast effects typically present below the 10 ps timescale), and the allowed frequencies are given by the matching boundary conditions\(^{(71,192)}\). In Figure 8, we present a calculation of the damped oscillation \(u(r = R)\) following heating of the Au sphere. The frequency content of the time-domain oscillation can be extracted by Fourier transform yielding a main frequency of \(\approx 40\) GHz, in agreement with the fundamental breathing mode expected for an object of size 2\(R = 80\) nm, with \(f = c_L/2R\)\(^{(70,248)}\) where \(c_L\) is the longitudinal sound velocity in Au. The calculation presented here considers water
as surrounding medium (commonly used in experiments, see, e.g., ref.[247]), however the technique is general and can be utilized for any surrounding elastic material.[192,241,248]

4.2.3. Experimental Imaging and Control of Coherent Phonons

In a pump-probe setup, the dynamics of the generated phonons can be extracted from the time domain signal measured by a probe pulse and described by a damped oscillator, see for example Figure 9a. Figure 9a(i) illustrates how a transmission type pump-probe experiment (depicted schematically in Figure 9a(ii)) allows to capture the diverse ultrafast phenomena. By also including the contribution from electrons, the damped oscillator of the previous example would exhibit a different phase value \( \phi \).[69] In fact, both contributions, electronic and lattice, are captured by the damped oscillator equation with a 90 degree phase difference, allowing to determine the fundamental mechanisms at play.[69–71,249] In Figure 9b, we illustrate this behavior by showing the results obtained in Perner et al.[239] for a transmission pump-probe experiment where the phase-quadrature contributions from each of the mechanisms in the pump-probe signal can be discerned.

Moreover, by using a precisely time delayed second pump pulse, it is also possible to generate oscillations with a specific phase relationship, leading to mode interference and selection, a strategy introduced in Del Fatti et al.[250] and demonstrated also in ref.[70]. One example was demonstrated by Yu et al.[243] where the generation of coherent phonons of a given frequency in Ag-core–shell nanoparticles have been demonstrated to be controlled by precisely timed ulterior control pulses (see Figure 9c).

Pump-probe experiments give access to a single parameter representation of phonon distribution, \( \Delta T/T \) or \( \Delta R/R \) (see, e.g., Figure 9c(iii)). Other techniques consider the use of an X-ray beam, instead of optical probes, to image the lattice displacement via diffraction, allowing to map the coherent phonon dynamics generated by optical pump pulses in Au nanoparticles at different times.[253] This technique produces 3D representations of the coherent phonon vibrations with ps resolution.

It has also been shown[244] that by tailoring plasmonic nanoantennas optical response through the modification of its geometry, specific phononic modes can be excited and controlled by light using different polarizations,[244,252] effectively coupling the optical and phononic response in nanostructures. Figure 9d shows the obtained phononic spectra as well as the utilized geometry in O’Brien et al.[244]. This approach had already been explored in ref.[245]. Figure 9e, where control over the phonon spectrum is achieved through mechanical constraints.[245,253] Additional coupling examples between plasmon and phonon modes were recently studied by Ahmed et al.[254] where a plasmonic resonance shift has been associated with the influence of excited phonon modes on the electric permittivity, thus highlighting the mechanical phonon contribution in molding the optical properties of nanostructures of different geometries and compositions.

5. Perspectives and Outlook

In this review we have explored recent developments across the fields of plasmonics and phononics, providing a ground for new developments at the plasmo-phononic intersection. We have particularly focused on light (photons) and phonon interaction in metals where electrons play a preponderant middle role between photons and phonons. Other direct interactions between light and phonons were not detailed since they typically play a minor role in plasmonic materials and in heat generation (e.g., SPhPs), but can be of larger importance in other materials. We have however briefly referred photon–phonon interactions also in non-plasmonic materials which play a major role in applications such as SPP–SPhP hybrids[85] and PhoXonic crystals.[255] In this review, we have also provided an outlook of recent achievements at the intersection between metallic plasmonics and phononics which can serve as road map for further developments both at a fundamental and applied level. We have finally summarized the theoretical frameworks exposed throughout the review in terms of modeling and design of devices and applications. In this section, we start with a brief discussion about photon-phonon applications non-metallic materials to highlight two exciting research areas at the intersection between phononics and plasmonics not explored so far in this review (SPP-SPhP hybrids and PhoXonic crystals) and proceed to highlight on plasmo-phononics by commenting on specific examples in the literature and identifying potential areas of future developments.

5.1. SPhP Nanophotonics and SPP-SPhPs Hybrids

In Section 2.2, we referred to the existence of SPhPs as a solution to Maxwell’s equations formally identical to SPPs.
Similarly, nanophotonic applications typically associated to SPPs and LSPs can be found for SPhPs in the mid-infrared range, such as biosensing using SiC,[81,256] metamaterial based absorbers/emitters[257] or synergies between plasmonic nanoantennas and SPhPs in Au nanostructures on top of SiC for plasmonic sensing in the IR.[258] Further interactions between...
plasmonics and phononics consider heterostructures of monolayer graphene/multilayer hBN that can support coupled SPP-SPhP modes\(^{[85]}\) for tunable nanophotonics sensors and emitters in the mid and far-infrared range. Detailed reviews regarding physical processes and applications are available in refs. \([32,79,85,86]\).

5.2. Phoxonic Crystals: Photons and Phonons in Dielectrics

In Section 3.2, we explored transport of phonons as waves and introduced the concept of phononic crystal as a periodic structure of material with different elastic properties which can give rise to a phononic bandgap, in analogy with a photonic crystal where a periodic structure of materials with different refractive indexes gives rise to a photonic bandgap. An interesting concept is a crystal where both the elastic properties and the refractive indexes lead to the existence of a bandgap for both photons and phonons provided that the dimensions of periodicity are properly engineered (e.g., periodic array of holes in a slab of transparent material, for example Si). This double-bandgap crystal (phononic and photonic) is called a PhoXonic crystal, first introduced by Maldovan and Thomas.\(^{[255,259]}\) If the periodicity is locally broken by introducing a defect (i.e., missing one hole in the array), a cavity can be formed. By properly engineering the crystal, modes that cannot propagate (due to the bandgap) can be confined in the defect. In this situation, photon and phonon modes occupy the same volume and direct interactions between the confined photons and phonons can be investigated. Similarly, waveguides for photons and/or phonons can be formed by aligning defects in lines or specific patterns. Photon–phonon interaction and coupling through this scheme was demonstrated for example in ref. \([260]\) in Si. Applications are varied\(^{[4]}\) and include nanomechanical oscillator cooling,\(^{[261]}\) ultrasensitive mass sensors,\(^{[260]}\) chemical and biochemical sensors,\(^{[262]}\) and gas/liquid sensors,\(^{[263]}\)

A dedicated review of physical processes and applications concerning phoxonic crystals is present in ref. \([264]\).

5.3. Plasmo-Phononics Applications

Most of the content in Sections 2–4.2 concerned plasmonics (with metals) and phononics. On a fundamental level, the coupling between plasmonic and phononic phenomena, their microscopic interactions and their influence on material properties can be investigated through pump-probe and Raman systems, opening the door to interesting fundamental studies of the photon–(electron)–phonon interaction.

From the applications point of view, contrary to electronic devices (where only electrons with energy close to the Fermi level play a role in transport), phonons (being bosons) can be excited in a broad range of frequencies, depending on their effective temperature. While the effective design of phononic devices is still in its infancy, the possibilities are vast. Heat generation is currently the main source of performance degradation for nanoelectronic devices\(^{[120,127]}\) and with current nm-scale fabrication below the phonon mean free path, new possibilities are envisaged for heat management through phonon propagation control.\(^{[39]}\) In this direction, a new class of thermal analogues of electronic devices have been recently introduced\(^{[265,266]}\) such as thermal diodes\(^{[267,268]}\), thermal transistors,\(^{[269]}\) thermal logic gates and memories,\(^{[270]}\) The possibility to tailor phonon generation described in Section 4.2, leaves room to conceive hybrid nanosystems comprising plasmonic elements where vibrational resonances (or heat generation) are sensitive to interactions with the environment. In particular, this strategy has promising implementations in cavity optomechanical systems.\(^{[271,272]}\) Prospective applications of these fundamental aspects fall into nanomechanical resonators,\(^{[273]}\) nanomechanical filters, new sensing and transduction devices\(^{[274]}\) and quantum information processing.\(^{[275]}\) Further applications hold promise in the study of biological elements, examples are depth profiling by monitoring elastic waves\(^{[276]}\) and photoacoustic imaging of cells with nanoparticles\(^{[277,278]}\) opening the door to medical imaging and diagnostics.

Recent studies are especially expanding in the direction of opto-thermo-mechanical systems where plasmonic elements enable the coupling of optics and mechanics with thermal degrees of freedom.\(^{[4,5,273,279–284]}\) One example of such system is presented by Zhu et al.\(^{[273]}\) where a photothermal optomechanical device composed of a Au metamaterial and a Fabry–Perot cavity is illuminated by a laser whose energy is converted into heat generating a photoinduced stress via a thermoelastic process consequently causing a change in the optical response. A characteristic light-induced back-action force, revealed through solving a system of three (optical-thermal-mechanical) coupled equations for the device, produces mechanical work by providing energy (amplification) to or removing energy (damping) from the mechanical oscillation mode.\(^{[285,286]}\) This concept enables the amplification (acoustic lasing) or cooling of mechanical vibrations. While working at modest frequencies (~200 kHz),\(^{[273]}\) the principle is a first-step toward high-speed acousto-optic light modulation in GHz-THz for telecommunication technologies. Another example\(^{[280]}\) concerns a electrostatically and thermally actuated nanoelectromechanical system where the plasmonic resonance mediates the optomechanical and thermomechanical coupling. The device is capable of electro-optic modulation, selective nanomechanical transduction, and mechanical lasing, constituting a promising building block for high spatial resolution light modulator arrays and tunable metasurfaces with applications in light-beamng, optical pulse and wavefront shaping. The effect of plasmonic heating has been also recently pushed to the atomic limit as in ref. \([284]\) where an optical memristor was realized exploiting the combined effect of optical, thermal and electrostatic effects in a metallic filament composed of a few atoms. These opto-thermo-mechanical devices set promising pathways for plasmo-phononics applications at the intersection between plasmonics and phononics.

5.4. Summary of Modeling Frameworks and Application Areas at the Intersection between Plasmonics and Phononics

In Figure 10, we summarize the exposition provided throughout this review regarding design tools to enable the engineering of plasmo-phonon applications. By looking at the time and length scales, one can choose the most appropriate modeling framework as a starting point for plasmo-phonon engineering and design, where the optical, thermal and mechanical degrees of freedom come into account.

In Figure 11, we provide an outlook of application areas and their intersections. In particular we illustrate with recent
Figure 10. Time scale versus length scale map of most appropriate modeling frameworks in plasmonics (optical-thermal domains) and phononics (thermal-mechanical domains). The boundaries between modeling frameworks are merely indicative of the length and time scales where the frameworks are typically applied (e.g., in steady-state, the BTE is not restricted to a particular time scale). The color code refers to optical, thermal and mechanical modeling domains, which are typically considered separately in the macroscale. In the microscale, optical-thermo-mechanical processes are fully taken into account by considering a first-principles approach (Schrödinger Equation $\hat{H} = \Psi E$ or Newton’s second law $m \frac{d^2x}{dt^2} = F$); in the macroscale, macroscopic equations are employed, with interaction terms accounting for the interactions at the intersection between the domains; in between micro- and macroscale, Boltzmann transport equation is typically employed.

Figure 11. Prospective application areas and examples of opto-thermo-mechanical devices lying at the intersection between plasmonics (optical-thermal domains) and phononics (thermal-mechanical domains). Center, application areas (and non-exhaustive application examples) of optical, thermal, and mechanical domains and their intersections. At the intersection between the optical and mechanical domains, we highlight radiation pressure devices such as optical tweezers[287] where the forces induced by the optical field allow to control the mechanical degrees of freedom. At the intersection between the optical and thermal domains, we highlight photothermal and thermoplasmatic devices where the thermal response of the system (heat and temperature) can be controlled by light (e.g., refs.[17, 103]); At the intersection between the thermal and mechanical domains, thermophononic applications are foreseen such as thermal and mechanical phononic crystals (e.g., refs. [19,21,199]) and phonon lasers (e.g., refs. [285,286, 288]); Examples of opto-thermo-mechanical devices at the intersection between the optical, thermal, and mechanical domains are represented in (a–d): a) An atomic optical memristor where optically controlled radiation, thermal, and electrical forces acting on an atomic junction of Ag produce a photoswitch, inset colored SEM image of the fabricated optical memristor. Reproduced with permission.[284] Copyright 2018, American Chemical Society; b) An optically driven nanomechanical resonator with a membrane consisting of plasmonic metamaterial formed by cross-shaped nanoslots etched in a Au membrane (inset, colored SEM image of the membrane with zoom at cross-shaped nanoslots). Reproduced with permission.[273] Copyright 2016, Springer Nature; c) A passive (zero input power) electromagnetic radiation sensor consisting in a nano electromechanical system integrating a plasmonic metasurface of Au patches of ~1 μm side (inset). Reproduced by permission.[282] Copyright 2017, Springer Nature; d) A optically induced thermally actuated (see inset) reconfigurable plasmonic metasurface consisting of C-shaped Au structures within SiN beams, SEM image. Reproduced with permission.[283] Copyright 2011, American Chemical Society.
experimental works which take advantage of the optical, thermal and mechanical degrees of freedom in applications such as optical switching (Figure 11a, [284]), optically controlled nanomechanical resonators with mechanical phonon lasing (Figure 11b, [273]), photothermal nanomechanical actuated passive sensors (Figure 11c, [282]), and photothermally controlled reconfigurable metasurfaces (Figure 11d, [283]).

6. Conclusion

In this review, we provided an overview of the basic theory and illustrated with recent theoretical and experimental works at the intersection between plasmonics and phononics. In particular, we reveal the role played by phonons in each of the two fields and provide a comprehensive map of the interactions between photons, electrons and phonons. The review aimed at offering a starting point for the design of systems and devices where thermal and mechanical degrees of freedom can be optically controlled and vice-versa, ultimately achieving opto-thermo-mechanical devices at the nanoscale and highlighted the potential benefits of engineering plasmo-phononic devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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