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Topical Review

Near-field radiative heat transfer in hyperbolic materials

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Abstract

In the post-Moore era, as the energy consumption of micro-nano electronic devices rapidly increases, near-field radiative heat transfer (NFRHT) with super-Planckian phenomena has gradually shown great potential for applications in efficient and ultrafast thermal modulation and energy conversion. Recently, hyperbolic materials, an important class of anisotropic materials with hyperbolic isofrequency contours, have been intensively investigated. As an exotic optical platform, hyperbolic materials bring tremendous new opportunities for NFRHT from theoretical advances to experimental designs. To date, there have been considerable achievements in NFRHT for hyperbolic materials, which range from the establishment of different unprecedented heat transport phenomena to various potential applications. This review concisely introduces the basic physics of NFRHT for hyperbolic materials, lays out the theoretical methods to address NFRHT for hyperbolic materials, and highlights unique behaviors as realized in different hyperbolic materials and the resulting applications. Finally, key challenges and opportunities of the NFRHT for hyperbolic materials in terms of fundamental physics, experimental validations, and potential applications are outlined and discussed.

Keywords: near-field radiative heat transfer, hyperbolic materials, photon tunneling, hyperbolic phonon polaritons

1. Introduction

As one of three pathways of heat transfer, radiative heat transfer is ubiquitous in nature and plays an important role in many different areas of science and engineering. For some time, the understanding of radiative heat transfer has focused on the well-known Stefan–Boltzmann law, which establishes a ceiling on radiative heat transfer between two bodies, i.e. \( Q = \sigma (T_1^4 - T_2^4) \), where \( \sigma \) is the Stefan–Boltzmann constant \([1]\). In such a law, the maximal heat flux between two objects only can be maintained at 6.12 W m\(^{-2}\) when the temperature of the hot emitter and cold receiver are 301 K and 300 K, respectively. However, such a low heat flux density can barely meet current cooling requirements for highly integrated micro-nano electromechanical devices. On the other
hand, the power output of thermophotovoltaic (TPV) systems is far weaker than thermoelectric systems and thermodynamic cycle technologies, which results in a limit on the widespread application in the field of recovered waste heat [2].

 Fortunately, the limit can be greatly overcome by bringing two objects in proximity at the near field; that is, distances smaller than the thermal wavelengths. In the near field, the coupling phenomenon of evanescent waves provides an additional channel for photon tunneling [3–5]. As a result, the near-field radiative heat transfer (NFRHT) can exceed the blackbody limit by orders of magnitude [6–9]. The significant radiative heat flux in the near field provides a new route for many potential applications [10, 11], such as TPV [12–23], thermal rectification [24–36], noncontact refrigeration [37–41], and thermal transistors [42]. As large heat fluxes are critical in such applications, continuous efforts have been devoted to highly efficient near-field heat transport.

Initially, the polar dielectric materials that support surface phonon polaritons (SPhPs), and the materials (metals, semiconductors, etc) that supporting surface plasmon polaritons (SPPs) were extensively investigated to enhance the NFRHT both theoretically and experimentally [43–57]. These strategies have largely explored the enhancement effects of isotropic surface polaritons (i.e. isotropic materials) on near-field thermal radiation. However, the enhancements are restricted to narrow frequency bands around the frequency of the surface mode resonance.

Hyperbolic materials are novel anisotropic materials with different dielectric properties along orthogonal directions, and have attracted enormous interest in the field of NFRHT in recent years due to their preeminent optical properties [58–60]. Their dispersion relations for electromagnetic waves show an open hyperboloid, which makes it possible to support propagating waves with high wavevector [61]. In 2012, Biehs et al showed that the broadband excitation of hyperbolic phonon polaritons (HPPs) in hyperbolic materials could greatly enhance the NFRHT, indicating that hyperbolic materials have great potential for NFRHT [62]. After this pioneering work, various hyperbolic materials were since explored to enhance the NFRHT.

Due to broadband excitations of surface polaritons and their unique optical properties, hyperbolic materials have great potential for a variety of applications. However, the phenomenon and physical mechanism of NFRHT in hyperbolic materials still need to be further studied. To broaden the understandings of hyperbolic materials and help define their role in potential applications, it is necessary to make a comprehensive overview of NFRHT in hyperbolic materials, summarize the current research results, and clarify research concepts, which will lay a foundation for further research. In this paper, the NFRHT in hyperbolic materials is reviewed, the related concepts and recent research progress are introduced. Applications of near-field radiation in hyperbolic materials, such as thermal switches and near-field TPVs (NTPVs), are also described.

2. Theory and methods

2.1. Introduction to hyperbolic materials

For non-magnetic materials, the response to electromagnetic waves can be described as a permittivity tensor, which is usually a $3 \times 3$ diagonal matrix diag($\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}$) [63]. When the three principal diagonal elements are equal, the material is called isotropic. The isotropic behavior of propagating waves leads to a spherical isofrequency contour described by the equation $k_x^2 + k_y^2 + k_z^2 = \omega^2/\varepsilon^2$ (figure 1(a)), where $k_x$, $k_y$, and $k_z$ are the x, y, and z components of the wavevector, $\omega$ is the wave frequency and $c$ is the speed of light. The closed sphere isofrequency contour in isotropic materials results in the finite wavevector of the propagating waves. As the energy carried by an electromagnetic wave is directly proportional to its wavevector, the limitations of wavevectors indicate that the thermal radiation of isotropic materials is finite.

Materials with larger electromagnetic wavevectors are desired to increase the radiative heat transfer. In recent years, researchers have found a class of materials for which the principal diagonal elements of dielectric tensor are not all the same sign [58–60]. For a transverse magnetic wave (TM polarized) in such medium, the isofrequency relation changes to $(k_x^2 + k_z^2)/\varepsilon_{\perp} + k_y^2/\varepsilon_{\parallel} = \omega^2/c^2$ Note the dielectric tensor is given by $\varepsilon = \sqrt{\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2}$, where $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\parallel}$ are the in-plane components, and $\varepsilon_{zz} = \varepsilon_{\perp}$ is the out-of-plane component. For such anisotropic materials, the spherical isofrequency contour distorts to an ellipsoid, when extreme anisotropy such that $\varepsilon_{\perp} \cdot \varepsilon_{\parallel} < 0$ exists, the isofrequency contour opens into an open hyperboloid (figures 1(b) and (c)). Therefore, this kind of materials are called hyperbolic materials. When one component of the dielectric tensor is negative ($\varepsilon_{xx} > 0, \varepsilon_{yy} > 0, \varepsilon_{zz} < 0$), it is called type I hyperbolic material, while two negative components ($\varepsilon_{xx} < 0, \varepsilon_{yy} < 0, \varepsilon_{zz} > 0$) for type II hyperbolic material. The openness of the isofrequency contour means the electromagnetic wavevector can be infinite. Therefore, electromagnetic waves in hyperbolic materials can carry more energy and lead to increased radiative heat transfer.

As an artificial subwavelength structure, hyperbolic metamaterials (HMMs) have many unusual optical properties. There are several forms of metamaterials to realize hyperbolic properties: layered metal-dielectric structures [67–70], nanowire arrays [71–76], arrays of metal-dielectric nanoparticles [64], graphene-based metamaterials [65, 77–79], and others (figures 1(d)–(g)). These anisotropic structured materials have unique properties that include strong enhancements in the spontaneous emission, divergence of the state density, negative refraction, and enhanced superlensing effects [79–83]. The divergence of the state density and special electromagnetic responses different from conventional media provide HMMs with great potential in the fields of super-resolution imaging, tunable radiative heat fluxes at the nanoscale, nanophotonic devices, and solar photovoltaics [58, 59].

However, for artificial HMMs, when the tangential wavevector component is larger than $\pi/\Lambda$ ($\Lambda$ is the unit metamaterial period), the hyperbolic dispersion is no longer
2.2. Fabrication of hyperbolic materials

In the fabrication of hyperbolic materials, some factors affecting the hyperbolic behavior, such as surface roughness, porosity, and filling fraction of materials, are the key factors to be considered. There have been some successful fabrication methods for reference, here is a brief overview.

2.2.1. Nanowire metamaterials. To fabricate nanowire structures, anodic alumina membrane can be used to grow the required templates to form a dielectric host substrate with periodic nanopores, in which silver (or gold) nanowires can be electrochemical deposited (figure 2(a)) [77, 93–96]. The nanowires can be grown by direct current electrodeposition from a thiosulfate bath [97, 98], or prepared by partially etching the anodic alumina membrane template in a NaOH solution [99]. The optical properties can be further improved by two-step anodizing and pre-pattern induced self-assembly [95]. The spacing of nanowires is determined by the anodizing conditions, but the pore size and diameter of nanowires are determined by pre-deposition etching. Compared to the optical wavelength used in the experiment, the lateral sizes and spacing between nanowires are smaller, so only the average value of nanowire parameters matters. The optical characteristics of nanowires could be stable relative to the fabrication tolerance [100, 101]. The silicon nanowires sample can be fabricated by using a mask made of polystyrene nanosphere array [102], the details on the transfer technique can be found in [103, 104].

2.2.2. Multilayer metamaterials. The fabrication of multilayer HMMS requires the deposition of ultra-thin and smooth metal/dielectric films (figure 2(b)). The materials behaving as metal can be surface deposited by electron beam evaporation [105, 106], low pressure chemical vapor deposition (CVD) [107], or be grown by molecular beam epitaxy (MBE) on lattice-matched substrates [108]. Dielectrics can be grown by plasma enhanced CVD [109]. The alternate plasmonic materials can be deposited by reactive sputtering or pulsed laser deposition [110]. The requirement of very uniform and smooth surface can be achieved through MBE, and the minor deviation of layer thickness will not significantly affect the effective medium response [111–113].

2.2.3. Natural hyperbolic materials. For natural hyperbolic materials, thin sheets are usually used. The hBN sheets could be obtained from hBN crystals or N-methyl-2-pyrrolidone (NMP) [66, 114, 115]. High-pressure/high-temperature method is often used for the growth of hBN crystals [116, 117]. The lateral sizes for hBN crystals in commercial powder are usually between hundreds of nanometers and tens of microns. The hBN sheets of lateral sizes similar to or smaller than crystal can be obtained by top-down approaches like mechanical exfoliation [118–122], sonication-assisted direct solvent exfoliation [123], chemical functionalization [124]; while the lateral sizes of hBN sheets from bottom-up approaches like CVD and non-epitaxial growths could be as large as a few centimeters (figures 2(d) and (e)) [125–127]. The α-MoO₃ sheets can also be obtained from MoO₃ powder, the commonly used method is thermal physical deposition method (figure 2(c)) [128, 129], and focused ion beam etching could be employed to meet the requirements [89].

2.3. Characterization of hyperbolic materials

The optical and morphology characterization of hyperbolic materials could be performed using Fourier transform infrared spectrometer [87], scanning transmission electron microscope [99, 102, 109], atomic force microscope...
the NFRHT between anisotropic plates can be expressed for these functions can be found in \[2\]. While the dyadic Green’s function is used to stochastic Maxwell’s equations and fluctuation-dissipation 2.4. Calculation formula for NFRHT The topological transition can be observed by time resolved Using the time correlated single photon counting technique, active refraction ability of hyperbolic materials \[2\]. Optical measurements can be made to characterize the negative refraction ability of hyperbolic materials \[95, 133\]. Using the time correlated single photon counting technique, the topological transition can be observed by time resolved photoluminescence \[106\].

\begin{align*}
\xi(\omega, \beta, \varphi) = & \begin{cases} 
\text{Tr} \left[ (I - R_z^2 T_z^1 T_z^2) \right], & \beta < k_0, \\
\text{Tr} \left[ (R_z^2 - R_z^1) D (R_z^1 - R_z^0) D^* \right] e^{-2|k_z|d}, & \beta < k_0
\end{cases}
\end{align*}

where \( \varphi \) is the azimuth angle, and \( \xi(\omega, \beta, \varphi) \) is the energy transmission coefficient, which can be expressed as:

\begin{equation}
Q = \frac{1}{8\pi} \int_0^{\infty} \int_0^{2\pi} \int_0^{\pi} \Theta(\omega, T_1) - \Theta(\omega, T_2) |d\omega| d\beta d\varphi,
\end{equation}

2.4. Calculation formula for NFRHT

The calculation of NFRHT depends primarily on the stochastic Maxwell’s equations and fluctuation-dissipation theory, while the dyadic Green’s function is used to express the electric and magnetic fields. The derivations for these functions can be found in \[4, 5, 134-136\], and the NFRHT between anisotropic plates can be expressed as:

\begin{equation}
R_{1,2} = \left[ \begin{array}{cc} r_{sp}^{(1,2)} & r_{pp}^{(1,2)} \\
r_{ps}^{(1,2)} & r_{pp}^{(1,2)} \end{array} \right], \quad T_{1,2} = \left[ \begin{array}{cc} t_{ps}^{(1,2)} & t_{pp}^{(1,2)} \\
t_{sp}^{(1,2)} & t_{pp}^{(1,2)} \end{array} \right],
\end{equation}

where \( r_{m,n} \) and \( t_{m,n} \) \((m = s, p; n = s, p)\) are the reflection and transmission coefficients from vacuum to the emitter or receiver, in which \( m \) and \( n \) represent the polarization state of the incident and reflected (transmitted) waves respectively, \( s \) and \( p \) indicate \( s \)-polarized and \( p \)-polarized plane waves. These coefficients can be obtained from the modified \( 4 \times 4 \) transfer matrix method described in the next section. The matrix \( \mathbf{D} \) is given as \( \mathbf{D} = (\mathbf{I} - \mathbf{R}_1 \mathbf{R}_2 e^{-2|k_z|d})^{-1} \). For isotropic materials, no polarization conversion occurs between two linearly polarized waves, so the off-diagonal elements in the transmission and
reflection coefficients are zero. However, the off-diagonal elements cannot be ignored for anisotropic materials.

2.4.1. The $4 \times 4$ transfer matrix method. To calculate NFRHT, the calculation for the reflection and transmission coefficients at different azimuth angles $\phi$ is needed, where $\phi$ is the angle at which the incident plane deviates from the $x$-$z$ plane. The permittivity tensor in the $x'y'z'$ coordinate system is expressed as [137]:

$$
\begin{pmatrix}
  \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\
  \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\
  \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz}
\end{pmatrix} = T_zT_z^{-1},
$$

(4)

where $T_z$ is the coordinate rotational transformation matrix, and $\varepsilon$ is the permittivity tensor in the coordinate system. The matrix of $T_z$ is:

$$
T_z = \begin{pmatrix}
  \cos \phi & \sin \phi & 0 \\
  -\sin \phi & \cos \phi & 0 \\
  0 & 0 & 1
\end{pmatrix}.
$$

(5)

This method was used in the analysis of Casimir interactions in anisotropic materials [138, 139]. Taking the TM incident wave as an example, the EM fields in the medium can be written according to the $x'y'z'$ coordinate system, as follows:

$$
H = U(z) \exp(j\omega t - j\beta x), \quad \text{where} \quad U = (U_x, U_y, U_z),
$$

(6)

$$
E = j(\mu_0/\varepsilon_0)^{1/2}S(z) \exp(j\omega t - j\beta x), \quad \text{where} \quad S = (S_x, S_y, S_z),
$$

(7)

where the superscript ' of the space variables was deleted for simplicity. Bringing equations (4), (6), and (7) into Maxwell’s equations, the following differential equations can be obtained:

$$
\frac{d}{dz}\begin{pmatrix}
  S_x \\
  S_y \\
  U_x \\
  U_y
\end{pmatrix} = k_0 A \begin{pmatrix}
  S_x \\
  S_y \\
  U_x \\
  U_y
\end{pmatrix},
$$

(8)

where the coefficient matrix is:

$$
A = \begin{bmatrix}
  jK_x\varepsilon_{xx}/\varepsilon_{zz} & jK_x\varepsilon_{xy}/\varepsilon_{zz} & 0 & K_x^2/\varepsilon_{zz} - 1 \\
  0 & 0 & 1 & 0 \\
  \varepsilon_{yz}\varepsilon_{xx}/\varepsilon_{zz} - \varepsilon_{yx} & \varepsilon_{yz}\varepsilon_{yy}/\varepsilon_{zz} + K_x^2 - \varepsilon_{zy} & 0 & -jK_x\varepsilon_{xz}/\varepsilon_{zz} \\
  \varepsilon_{zx} - \varepsilon_{xz}\varepsilon_{xx}/\varepsilon_{zz} & \varepsilon_{zx} - \varepsilon_{xx}\varepsilon_{yz}/\varepsilon_{zz} & jK_x\varepsilon_{xz}/\varepsilon_{zz}
\end{bmatrix}.
$$

(9)

It was shown that the heat flux between SiC nanowire arrays could reach 36 times that between SiC plates at the same temperature.

3. NFRHT of hyperbolic materials

3.1. NFRHT of hyperbolic metamaterials (HMMs)

The broadband excitation of phonon polaritons in hyperbolic metamaterials promotes significant photon tunneling, which results in super-Planckian thermal radiation. In 2012, Bihe et al first studied the NFRHT of hyperbolic materials [62]. They considered the NFRHT between HMMs composed of periodic SiC nanowire arrays, where the optical axis is vertical to the material surface (figures 3(a) and (b)). These media could support frustrated modes that transport heat via photon tunneling. In particular, the frustrated modes can be supported in a broadband spectrum, resulting in larger heat fluxes compared with those generated by the narrowband coupled surface polariton modes. The frustrated modes supported by HPPs are demonstrated to achieve perfect transmission for wavevectors smaller than $1/2d$, which significantly enhances the NFRHT. In particular, the frustrated modes can be supported in a broadband spectrum, resulting in larger heat fluxes compared with those generated by the narrowband coupled surface polariton modes. The frustrated modes supported by HPPs are demonstrated to achieve perfect transmission for wavevectors smaller than $1/2d$, which significantly enhances the NFRHT.

3.1.1. Nanowire/nanohole array structures. After the work of [62], many theoretical works on the NFRHT of various nanowire and nanohole array structure HMMs were performed. Basu and Wang [140] studied the NFRHT between doped Si nanowire array HMMs, and found that the heat flux between doped Si nanowire arrays can be nearly three times that between two doped Si plates with a vacuum gap of 20 nm. Liu et al [141] investigated the NFRHT between two doped Si nanowire/nanohole array HMMs and found that the heat flux of both configurations are more than one order of magnitude stronger than that of bulk doped Si, the enhancement of nanowire arrays is larger than that of nanohole arrays. Liu et al [142] studied the NFRHT of doped Si nanowire/nanohole HMMs and showed that the heat flux between Si nanohole arrays at submicron gap was nearly eight times larger than that between Si plates, and that of Si nanowire arrays was approximately 12 times larger than Si plates (figures 3(c)–(f)). Liu and Shen [143] described an HMM made of metal wire arrays and observed that the heat flux between a gold nanowire array and a SiC plate is much greater than that between a gold plate and a SiC plate. Lang et al [144] found that...
GaN/Ge nanowire HMMs have a larger penetration depth of thermal photons than semi-infinite phonon-polaritonic media, which gives a preferred NFRHT. Bihs et al [145] studied the NFRHT between two SiC nanoporous materials and found that the air inclusions can significantly enhance the heat flux, which is explained by the appearance of additional surface waves and frustrated modes in a wide spectral range. Liu et al [146] investigated the NFRHT between carbon nanotube arrays and predicted that at any vacuum gap distance, the heat flux could be enhanced compared to that between SiC plates. At a gap distance of 10 nm, the heat flux is approximately ten times greater (figures 3(g) and (h)).

3.1.2. Periodic layered structure. In studies on NFRHT, periodic layered structures are another common form of HMMs (figure 4). Guo et al [147] proposed an HMM made from periodic layered SiC/SiO\(_2\) and calculated the super-Planckian radiation heat flux using effective medium theory. Bihs et al [148] used scattering-matrix calculations to determine the heat flux of SiC/SiO\(_2\)-layered HMMs and arrived at the same conclusions. They showed that the layer thickness determines the wavevector cutoff for the Bloch band (figures 4(b) and (c)). Lang et al [144] investigated the NFRHT between GaN/Ge layered HMMs and revealed a significantly enhanced heat flux due to the large penetration depth of thermal photons (figures 4(d) and (e)). Liu et al [142] found that the NFRHT between D-Si/Ge layered HMMs can significantly exceed the blackbody limit. In the far-field, the heat flux between D-Si/Ge layered HMMs is nearly twice as large as that between bulk materials (figure 4(f)). Bihs and Ben-Abdallah [149] studied the NFRHT between SiC/Ge layered HMMs and showed that regardless of whether the top layer is SiC or Ge, the heat flux can significantly exceed the blackbody limit but is stronger when SiC is the top layer. Song et al [150] studied the NFRHT between periodic layered HMMs consisting of a magneto-optical material (InSb) and a dielectric (SiO\(_2\)). They observed an enhanced heat flux due to hyperbolic modes and introduced the induction of the hyperbolic modes from an external magnetic field.

3.1.3. Two-dimensional (2D) materials. Two-dimensional (2D) materials, such as black phosphorus (BP) and graphene, have attracted significant attention due to their excellent optical properties [50, 151–153]. Such 2D materials can produce a large number of resonances and provide channels for photon tunneling, and show a nice tunability. Patterning the 2D material sheet into metasurface will open the dispersion to become hyperbolic. The excitation of hyperbolic plasmons has led to enhanced radiative heat flux (figure 5). Liu and Zhang [154] proposed a hyperbolic metasurface (HMS) based on periodic graphene ribbon arrays. They revealed that the coupling between high wavevector evanescent waves and hyperbolic graphene plasmons could increase the NFRHT between the HMS by more than one order of magnitude compared to that of graphene sheets (figures 5(c) and (d)). Zhou et al [155] discovered that when a drift current is applied to graphene ribbons, the hyperbolic mode evolves into an extremely asymmetric shape. Yi et al [156] proposed an HMS based on narrow BP ribbons and found the NFRHT between HMS sheets can be significantly enhanced at high electron doping levels compared to that of BP sheets. Liu et al [157] investigated the NFRHT of BP gratings considering different patterning and electronic doping approaches. The BP grating was found to produce a higher heat flux by as much as 65% compared with its planar counterparts (figure 5(b)). Shen et al [158] studied the NFRHT of mono/multilayer BP and found that the heat...
Figure 4. (a) Sketch of multilayer HMM. Reprinted figure with permission from [150], Copyright (2020) by the American Physical Society. (b) Heat transfer coefficient for the SiC–SiO$_2$ multilayer HMM with passive materials as the topmost layer at various thicknesses. (c) Energy transmission coefficient of a SiC–SiO$_2$ multilayer HMM for 100 nm thick layers and $d = 10$ nm. Reprinted from [148], with the permission of AIP Publishing. (d) Heat transfer coefficient varying with the vacuum gap for a GaN/Ge multilayer HMM compared to other configurations. (e) Spectral penetration depth (solid) and heat transfer coefficient (dashed) for GaN/Ge multilayer HMMs at $d = 10$ nm. Reprinted from [144], with the permission of AIP Publishing. (f) Energy transmission coefficient for a D-Si/Ge multilayer HMM at $d = 10$ nm. Reprinted from [142], Copyright (2014), with permission from Elsevier.

Figure 5. (a) Schematic of NFRHT between two graphene gratings composed of arrays of ribbons. [155] (2020), reprinted by permission of the publisher (Taylor & Francis Ltd, www.tandfonline.com,). (b) Schematic of the NFRHT between nanostructured BP layers. [157] (2019), reprinted by permission of the publisher (Taylor & Francis Ltd, www.tandfonline.com,). Energy transmission coefficient at $\omega = 5 \times 10^{13}$ rad s$^{-1}$ for (c) graphene sheets and (d) graphene ribbon arrays at $d = 50$ nm. Reprinted from [154], with the permission of AIP Publishing. Energy transmission coefficient at $\omega = 5.5 \times 10^{13}$ rad s$^{-1}$ for monolayer BP with (e) $\mu = 1$ eV and (f) $\mu = 2$ eV at $d = 50$ nm. Reprinted from [158], Copyright (2018), with permission from Elsevier.
flux of monolayer BP could exceed that of blackbodies by three orders of magnitude, which was 18.5% higher than the heat flux of optimized graphene sheets (figures 5(e) and (f)).

3.2. NFRHT of natural hyperbolic materials

3.2.1. Uniaxial natural hyperbolic materials. Some uniaxial van der Waals crystals have natural hyperbolic properties. For example, in the infrared region, graphite can support broadband type II hyperbolic dispersion [146]. Shen et al [159] demonstrated the enhancement effect of non-resonant type II hyperbolic modes to NFRHT in graphite plates. After patterning graphite gratings, the material dispersion of graphite changes from type II to type I. For the case of optical axes in plane and perpendicular to the etching direction, non-resonant type I hyperbolic modes dominate the NFRHT, the heat flux is seven-fold larger than the counterpart plates and outperforms blackbodies by over four orders of magnitude (figures 6(a) and (b)). In the mid infrared region, calcite has two Reststrahlen bands with type I and type II hyperbolic dispersion, respectively. Salihoglu et al [160] carried out analyses on NFRHT of calcite, and compared to that of SiC. Their study revealed that the high-wavevector modes within the hyperbolic bands lead to the largely enhanced NFRHT of calcite.

Hexagonal BN (hBN) is a common natural hyperbolic material. In two infrared Reststrahlen bands where the permittivity tenses are opposite (\(\varepsilon_\parallel < 0, \varepsilon_\perp > 0\) in type I hyperbolic band, \(\varepsilon_\parallel > 0, \varepsilon_\perp < 0\) in type II hyperbolic band), hBN can support many phonon-polaritonic waveguide modes [130–132, 162]. Liu and Xuan [161] considered the NFRHT between two hBN films with the optical axis parallel to the surface and identified the excitation of hyperbolic SPhPs (HSPPs) for the first time (figures 6(c)–(f)). As seen in figure 6(d), the main contributions of the radiation heat flux originate from the two hyperbolic bands. As a result, the NFRHT between bulk hBN slabs could be 120 times larger than the blackbody limit. Thus, HSPPs are demonstrated to enhance the NFRHT.

Wu and Fu [163] further studied the phonon polaritons of hBN and distinguished the roles for two kinds of HPPs: HSPPs and hyperbolic volume phonon polaritons (HVPPs). The HVPPs are essentially Fabry–Pérot resonances, which are propagating waves in the medium; while HSPPs are surface waves, which are evanescent waves in the medium. It was shown that when the optical axis is perpendicular to the medium surface, only HVPPs can be excited in the two hyperbolic bands (figures 7(a), (c), and (d)). When the optical axis is parallel to the medium surface, there are HVPPs excited in type I hyperbolic band, while both HVPPs and HSPPs excited in type II hyperbolic band (figures 7(b), (e), and (f)). Further research shows that in ultra-thin hyperbolic slabs, the dispersion curves of HVPPs and HSPPs can be smoothly connected [164]. In particular, the topology of HVPPs can be convex, flat, as well as concave, and can be regulated by adjusting the thickness of the hyperbolic slab, as seen in figures 7(g) and (h).

For hBN, the effects of the optical axis orientation and slab thickness were also discussed. For example, the absorption in a hBN slab could be manipulated by adjusting the tilted angle of its optical axis [165]. As the optical axis deviates from...
normal, the emissivity decreases in the type I hyperbolic band and increases in the type II hyperbolic band [166]. As the tilting angle increases, the wavevector of electromagnetic waves decreases and leads to a reduced radiation heat flux [137]. With the decrease of thickness, the excitation of HVPPs becomes dispersed [163]. Variations in the radiation heat flux and the topological shape of phonon polaritons open up new ways to clarify the mechanism and manipulation method of NFRHT in hyperbolic materials [167].

3.2.2. Biaxial natural hyperbolic materials. Biaxial hyperbolic crystals (such as \(\alpha\)-MoO\(_3\)) show different optical responses along their three crystalline directions, their hyperbolicity will become more complicated than uniaxial crystals [89–91]. The \(\alpha\)-MoO\(_3\) crystal has three Reststrahlen bands, there are \(\varepsilon_{xx} > 0, \varepsilon_{yy} < 0, \varepsilon_{zz} > 0\) and \(\varepsilon_{xx} > 0, \varepsilon_{yy} > 0, \varepsilon_{zz} < 0\) in band 1, 2 and 3 respectively (figure 8(b)). The regions for phonon polariton excitation are determined from the signs of the three permittivity components (figure 8(c)) [168]. Wu et al [169] studied the NFRHT between two \(\alpha\)-MoO\(_3\) biaxial crystals, it is observed that different crystal orientations will produce varying results (figure 8(d)). Due to the HVPPs excitation inside \(\alpha\)-MoO\(_3\) and HSPPs at the vacuum/\(\alpha\)-MoO\(_3\) interface, the NFRHT between two semi-infinite \(\alpha\)-MoO\(_3\) crystals is significantly enhanced. At a vacuum gap of 20 nm, the NFRHF can be larger than 2200 kW m\(^{-2}\) when the heat flux is along the [001] crystalline direction, which is much larger than between two hBN uniaxial crystals (figures 8(e) and (f)). In addition, based on the in-plane anisotropy, the NFRHT can be well controlled by relative rotation. Thus, biaxial natural hyperbolic materials have the potential for NFRHT as their special properties give a multitude of possible applications of interest.

3.3. NFRHT of 2D material/hyperbolic material heterostructures

It has been confirmed that the combination of graphene and dielectric (or metal) materials can produce coupling of graphene plasmons and other SPhPs (or SPPs), which leads to further mediation of the NFRHT [170–175]. However, the near-unity photon tunneling probability only appears over a narrow frequency range of exciting coupled SPhPs or SPPs, thus the frequency range of NFRHT enhancement is limited. Hyperbolic materials support broadband excitation of surface polaritons and have large energy transmission coefficients over a wide range of wavevectors. Therefore, the combination of graphene and hyperbolic materials produces new effects that are worthy of study.

Liu et al [176] investigated the NFRHT between graphene-coated doped Si nanowires (figures 9(a) and (b)), and theoretically demonstrated that the hybridization of graphene plasmons and hyperbolic modes cause a near-uniform photon tunneling probability over a wide frequency domain and large wavevector space. Thus, the NFRHT increases significantly and reaches 80% of the theoretical limit for hyperbolic materials. Besides, the NFRHT of graphene-coated metamaterials can be actively regulated by modulating the graphene chemical potential [177].

Combining uniaxial natural hyperbolic materials and graphene to form heterostructures could produce new hybrid polaritons in the mid-infrared band [137, 162, 178, 179].
After adjusting the chemical potential of graphene, the coupling ability of phonon-plasmon polaritons changes significantly, which illustrates a strong tunability \[180, 181\]. Zhao and Zhang \[182\] studied the NFRHT in graphene/hBN heterostructures, they found that graphene plasmons can be coupled with phonon polarons in hBN films, and produce two hybrid
Specifically, HPPPs always suppress the heat flux while SPPPs according to the chemical potential of graphene. More specifically, the spectral heat flux can be enhanced or suppressed by adding graphene plasmonic and phonon polaritons in hyperbolic materials. They demonstrated that the total heat flux can be significantly enhanced due to the coupling between graphene plasmon–phonon polaritons (HPPPs) produced from the coupling of SPPs and HSPPs, and hyperbolic plasmon–phonon polaritons (HPPPs) produced from the coupling of SPPs and HVPPs. HPPPs maintain the features of hyperbolic-waveguide-mode and could suppress the heat transfer, while SPPPs could enhance the heat transfer. Due to the coupling of polaritons, the total heat flux between graphene/hBN heterostructures can be greatly enhanced compared to bare hBN films or graphene monolayers, and can exceed the blackbody limit by three orders of magnitude (figure 9(d)). The periodic multilayer graphene/hBN structures can give rise to a further effective hyperbolic behavior, in addition to the intrinsic natural hyperbolic behavior of hBN [183]. The NFRHT could be actively modulated by changing the graphene chemical potential or through the number of graphene layers. Shi et al [184] found that heterostructures composed of five or more graphene-hBN cells perform better than other structures (figure 9(c)), the heat flux of infinite-cell heterostructure could be 1.87- and 2.94-fold larger than that of sandwich and monolayer structures, and exceed the blackbody limit by four orders of magnitude.

While biaxial natural hyperbolic materials like $\alpha$-MoO$_3$ exhibit excellent NFRHT performances, there are few studies on the combination of $\alpha$-MoO$_3$ and graphene. Wu et al [168] investigated the NFRHT between graphene-coated $\alpha$-MoO$_3$. They demonstrated that the total heat flux can be significantly enhanced due to the coupling between graphene plasmons and phonon polaritons in $\alpha$-MoO$_3$. In the Reststrahlen bands, the spectral heat flux can be enhanced or suppressed according to the chemical potential of graphene. More specifically, HPPPs always suppress the heat flux while SPPPs can enhance or suppress it, depending on the frequency [185]. Take the angular frequencies of 1.82 × 10$^{14}$ rad s$^{-1}$ as an example, for bulk $\alpha$-MoO$_3$, the heat flux contributions from HSPPs and HVPPs are 5.66 and 3.51 nJ m$^{-2}$ rad$^{-1}$ respectively. After covering graphene, the contributions of hybrid polaritons decreases (figures 9(f) and (g)). It can be seen that after coating graphene to hyperbolic materials, though the total heat flux can be enhanced, the relative size of spectral heat flux is variable.

In summary, hyperbolic materials have great potential to enhance NFRHT. Heterostructures of graphene and hyperbolic materials will bring more significant enhancements, which may have guiding significance in the designs of NFRHT experimental devices.

### 3.4. Experimental measurements

The experimental measurement and verification of the super-Planckian heat flux between two objects will provide a reliable basis for theoretical research, so it has always been the focus of academic attention. In the early stages, due to the difficulty of maintaining the nano-spacing and parallelism between two plates, the experimental configurations are mostly probe-substrate [186–189] or sphere-plate structures (figure 10(a)) [52, 190–194]. In recent years, due to the progress of technology, a number of experiments of plate-plate structure have emerged (figure 10(b)) [6, 9, 45, 56, 195–208]. The methods of controlling the parallelism and spacing of two plates can be divided into four categories: (a) separation by nanosphere/nanocolumn [6, 8, 9, 56, 202, 205, 208], (b) judging by the on-off of electrical signals [45, 196, 204], (c)
using the change of signal strength and interference fringes of transmitted/reflected light [201, 206, 209], and (d) using the correlation between capacitance electrode spacing and capacitance [195, 199, 207]. The temperature of the plates can be measured by embedding a temperature sensor/thermistor/thermocouple in the carrier loaded with the sample sheet [8, 9, 45, 56, 196, 199, 202, 204–208], or preparing a Pt electrode on the surface of the sample, and the temperature can be determined by the relationship between the change of resistance and temperature [188, 194, 197, 198, 200, 201, 203]. The measurement of heat flux can be achieved by heat flux meter, or by using the change of measured power and temperature in far-field and near-field to convert the heat flux [9, 45, 195, 198, 203, 204, 206–208]. The techniques used in the existing NFRHT experiments will provide reference and basis for the measurement of super-Planck heat flux of hyperbolic materials.

In recent years, the NFRHT of HMMs has also been experimentally studied. Shi et al [99] demonstrated a broadband thermal energy extraction device based on nickel nanowire HMMs (figures 10(c) and (d)). The thermal extractor made of HMMs acts as a transparent pipe to guide the radiative energy from the emitter without absorbing or emitting any radiation. They observed that compared to the case without thermal extractor, the NFRHT with HMMs thermal extractor can be enhanced by around one order of magnitude. Lim et al [107] measured the NFRHT between metallo-dielectric multilayer HMMs. The HMMs are made of alternating Ti and MgF2, and the active heat transfer area is 7.56 mm2 (figures 10(e) and (f)). They fabricated an integrated platform, and used a three-axis nanopositioner to locate the plate, the parallel of the plate is realized by capacitive sensing. With an Au temperature sensor placed on the back of the receiver component and a thermometer attached to the heat sink, the heat flux could be measured. The NFRHT between multilayer HMMs at d = 160 nm was increased by about 100 times compared to the far-field case, and was equivalent to that between bulk Ti media at d = 75 nm. Du et al [102] fabricated two 2 × 2 cm2 HMMs made of silicon nanorod arrays and studied their NFRHT using a home-made setup (figure 10(g)). The emitter and receiver are separated by four AZ photoresist pillars to keep parallel. The heat flux is measured by a differential way, i.e. subtracting the background dissipation from the input power. At the 500 nm vacuum gap, a strong heat flux density of 830 W m−2 was observed, which is 4.7 times larger than the blackbody value.

4. Applications

4.1. Twistable thermal switch

In recent years, the requirements of thermal information processing, thermal management, and thermoelectric conversion have drawn attention to the manipulation of heat flux as analogous to that of electric currents, such as a thermal switch. Many researches focused on thermal modulations for heat conduction through engineering phonon transport [210–212]. However, the phonon transmission speed is much lower, and the inevitable existence of local Kapitza resistance dramatically reduces the phononic heat flow. In Recent years, photon-based thermal transistors have attracted much attention because photons travel faster and can be used in non-contact applications [42, 213–215]. The relative rotation between the emitter and receiver can regulate the electromagnetic interactions between their interfaces [216, 217]. This effect symbolizes the adjustability of NFRHT, which can be used for twistable thermal switches [170, 218–224].

In 2011, Biehs et al [225] proposed to modulate the NFRHT by rotating two polar-metallic gratings around the heat flux direction (figures 11(a) and (b)). The results showed that at room temperature, the net heat flux could be modulated by up to 90%. Other materials were subsequently investigated to control the NFRHT by relative rotations, and the role of hyperbolic modes in twistable thermal switches was explored. Luo et al [226] studied the NFRHT between two twisted finite size polar dielectric nanoparticle gratings. Because of the size effect of square and circular gratings, changing the twisting angle will lead to significant oscillations of heat flux (figure 11(c)). Ge et al [227] studied the NFRHT between two suspended 2D anisotropic materials and observed that relative twisting of the upper and bottom sheets caused nearly four-fold differences in heat flux. He et al [228] realized the magnetoplasmodynamic manipulation of NFRHT using two twisted graphene gratings and observed that the magnetic field makes the grating have higher NFRHT modulation ability (by changing the graphene filling factor and twisted angles) compared with the zero field case (figures 11(d)–(f)). After covering graphene gratings with isotropic material slabs, the NFRHT was increased by approximately 150% and decreased by around 30% via mechanical twisting compared to that of bare slabs [229]. The twistable thermal switch composed of BP gratings was also proposed, the optimized switching factors could reach 90% at a gap distance of 50 nm, in the far-field regime, the switching factors could also be more than 70% at a gap distance of 1 μm [230].

Grating fabrication will be a significant challenge to provide modulators with good performances at nanometer gaps because the roughness and defects must be within a few nanometers. However, natural hyperbolic materials can be directly used for thermal modulation without patterning. Liu et al [231] proposed a pattern-free thermal modulator based on mechanical rotations between two hBN films with optical axes parallel to their surfaces (figures 12(a)–(c)). They found that the mismatch of type I HSPPs between two films enabled the hBN films to support a large modulation contrast. At a gap distance of 10 nm, the modulation contrast could be more than 5 for 1 nm thick films. Unlike uniaxial hyperbolic crystals which exhibit in-plane anisotropy only with the optical axis parallel to the surface, biaxial hyperbolic crystal α-MoO3 naturally exhibits both out-of-plane and in-plane anisotropy. In twisted α-MoO3, the highly anisotropic hyperbolic polaritons will produce electromagnetic interaction, which is conducive to rotational thermal modulation [234]. Wu et al [169] investigated the effects of relative rotations between two α-MoO3 films and found that the heat flux varies significantly due to misalignments of the HPPs inside α-MoO3 and HSPPs at the vacuum/α-MoO3 interfaces. When the heat flux was along the [010] direction, the modulation contrast can reach 2. Based on this work, the thermal modulation by relative rotations
between hBN and α-MoO$_3$ was also studied (figures 12(d) and (e)) [232]. It was found that the mismatch of HVPPs in the emitter and receiver leads to large modulation contrasts. By optimizing the thickness of the slabs, the modulation contrast can be up to 12.45, which is the highest known value. The unique electromagnetic properties of hyperbolic materials have great application potential in thermal modulations. The manipulation of NFRHT will open new ways for thermal management in microelectronic devices.

4.2. Near-field thermophotovoltaic (NTPV)

TPVs are a pollution-free and multi-purpose thermoelectric conversion device without moving parts, which can use a variety of heat sources. A TPV is composed of thermal emitters and low-bandgap photovoltaic cells. Semiconductor photovoltaic cells generate electron–hole pairs through electron valence band transitions based on incident photon radiation and directly convert the thermal energy into electricity. The energy conversion efficiency of TPV is limited by the Shockley–Queisser limit with a maximum of 41% [233]. However, when the distance between the emitter and the cell is less than the thermal wavelength, the dramatically increased energy transmission generated by NFRHT can significantly improve the efficiency of NTPV and even break the Shockley–Queisser limit. Therefore, NFRHT has inspiring potential in TPV applications.

There have been some explorations of NTPVs using conventional materials that reduce the vacuum distance to the nanometer level for increased efficiencies [12–23]. Hyperbolic materials are ideal high-temperature heat sources because of their large wavevector transmission characteristics. This has naturally led to their use in NTPVs to improve the output power. Vongsoasup et al [235] proposed an HMM radiator made of 2D tungsten grating that supports hyperbolic modes, and found that with the HMM radiator, the energy absorbed by the cell is enhanced compared to isotropic radiator (figure 13(a)). The maximum power output and conversion efficiency could reach 4.28×10$^5$ W m$^{-2}$ and 35%, respectively. Mirmoosa et al [236] theoretically show that NTPV system include tungsten nanowires allow the frequency-selective super-Planckian spectrum of thermal radiation, thus lead to efficient power generation, the power output per unit area can reach 3.3–4.3 W cm$^{-2}$. Chang et al [237] proposed an HMM composed of tungsten nanowire arrays embedded in Al$_2$O$_3$ as thermal emitter (figure 13(b)). They showed that at the vacuum gap of 20 nm, the output power of a semi-infinite HMM thermal emitter is 2.15 times greater than that of pure...
tungsten, and the energy conversion efficiency increased from 17.7% to 31.1% when using a limited thickness cell. Yu et al [238] investigated the NFRHT for an NTPV consisting of a plasmonic emitter and GaSb absorber with nanowire/nanohole arrays (figure 13(c)). Compared to the efficiency of 14.6% in planar GaSb system, the optimal efficiency of proposed system was up to 26.0%, and the power enhancement could up to a maximum of 78.3%. Jiang et al [239] proposed a NTPV composed of a tungsten nanowire HMM emitter and a two-junction tandem cell, the system can generate a power output of $4.7236 \times 10^6$ W m$^{-2}$ and the conversion efficiency can reach 45.26%, achieving 1.3 (2.38) times more electricity with 15.3% (25.95%) higher conversion efficiency than the single InGaAsSb (InAs) cell.

Jin et al [244] proposed using multilayer metamaterials formed alternately by tungsten and SiO$_2$ as the thermal emitter. At a vacuum gap of 100 nm, the output power was increased approximately six-fold compared to the case of a conventional tungsten emitter. Mirmoosa et al [240] proposed a germanium/tungsten-multilayer-based emitter (figure 13(d)) that achieved a large ultimate efficiency of more than 50% and radiative heat flux of about 200 kW m$^{-2}$. Lim et al [241] used doped Si/SiO$_2$-multilayer-based emitter (figure 13(e)) and coated multilayer graphene/SiO$_2$ on the cell. Compared with the system with bulk emitter and bare cell, the power output of the system is 24.2-fold enhanced. Ghanekar et al [243] chose a stack of alternating ZrC and SiO$_2$ thin films as the HMM in place of a bulk metallic heat sink. It was found that the presence of hyperbolic modes created additional NFRHT channels, which led to a sevenfold increased power density.

Combining 2D materials with natural hyperbolic materials to modulate the NFRHT between the emitter and cell allows optimizing the NTPV performance. Messina et al [12] proposed a kind of NTPV with an hBN emitter and an InSb cell coated with graphene. The calculation results showed that the cell efficiency and generated current are improved when InSb cell is coated with graphene, the system efficiency can reach 20% at a vacuum gap of 16 nm and graphene chemical potential of 0.5 eV. Wang et al [242] studied the performance of NTPV with both hBN emitters and InSb cells coated with graphene (figure 13(f)). The highest output electric power reached $7.6 \times 10^4$ W m$^{-2}$, while the highest energy efficiency was 34% for the system with a heterostructure emitter and uncoated cell. With graphene/hBN/graphene sandwiched structure as the emitter and uncoated InSb cell, the optimal output power density can reach $1.3 \times 10^5$ W m$^{-2}$ and the energy efficiency can be as large as 42% of the Carnot efficiency [245].
Though natural hyperbolic materials have unique advantages in NFRHT, the natural Reststrahlen bands are difficult to change due to their inherent lattice structure, which limits the spectral selection for NTPV. To overcome this limitation, the performance of natural hyperbolic materials in NTPV can be improved by coating with graphene or tilting the optical axis, which will be explored in the future. The application of HMMs in NTPVs has a strong development space with more forms of metamaterials that can bring new possibilities for NTPVs. In summary, improving the output power and efficiency of NTPVs can be achieved using the important class of hyperbolic materials.

5. Summary and prospects

The NFRHT of hyperbolic materials is introduced and reviewed. We first introduce the optical properties of hyperbolic materials and review their origin and development. The established calculation models for the NFRHT in hyperbolic materials are then introduced. After introducing the basic concepts of NFRHT for hyperbolic materials, we review the theoretical and experimental research progress of super Planck thermal radiation in hyperbolic materials, which includes metamaterials, 2D materials, and natural hyperbolic materials. In addition, we discuss the NFRHT of heterostructures that consist of 2D and hyperbolic materials. Finally, we introduce the application of NFRHT for hyperbolic materials, such as twistable thermal switches and NTPVs. The summary of this review helps to sort out the research content for the NFRHT in hyperbolic materials and lays a foundation for further research.

As the NFRHT of hyperbolic materials is rich in physics and has become increasingly practical, we anticipate that hyperbolic materials will continue to promote theoretical and technological development for NFRHT, and will play a crucial role in micro/nano thermal modulation and next-generation energy conversion systems. However, despite the extraordinary evolution of NFRHT in hyperbolic materials, there still exist plentiful fascinating phenomena and promising opportunities in both fundamental advances and practical applications.

(a) For theoretical works, although research on the NFRHT mechanisms in hyperbolic materials is relatively mature, there are still some challenges. To date, focus has been limited to the hybrid effects between hyperbolic materials and isotropic polaritons, but the hybrid phenomenon between hyperbolic materials and other anisotropic polaritons has rarely been considered. In addition, the hyperbolic effect of pseudo-periodic artificial metamaterials on the NFRHT has not been explored. Finally, the limit of NFRHT that hyperbolic materials can support has not been determined.

(b) For experimental works, many theoretical results and concepts require experimental verification, which may revolutionize the study of NFRHT. This includes hBN and other uniaxial anisotropic materials. Most importantly, in NFRHT experiments, research on hyperbolic anisotropic surface polaritons and the hybrid effects of hyperbolic polaritons is still missing.

(c) For practical applications, devices composed of hyperbolic materials are still in the concept stage, and there
is a long way to go into realistic production and life. In addition, as hyperbolic waveguides can transmit evanescent wave energy over long distances, it is an open question of whether hyperbolic materials can help break the strict requirements for heat transfer distances with near-field radiation, which reduces the processing costs and difficulty of these applications.

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