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Nonreciprocal thermal metamaterials: Methods and applications

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Abstract: Nonreciprocity of thermal metamaterials has significant application prospects in isolation protection, unidirectional transmission, and energy harvesting. However, due to the inherent isotropic diffusion law of heat flow, it is extremely difficult to achieve nonreciprocity of heat transfer. This review presents the recent developments in thermal nonreciprocity and explores the fundamental theories, which underpin the design of nonreciprocal thermal metamaterials, i.e., the Onsager reciprocity theorem. Next, three methods for achieving nonreciprocal metamaterials in the thermal field are elucidated, namely, nonlinearity, spatiotemporal modulation, and angular momentum bias, and the applications of nonreciprocal thermal metamaterials are outlined. We also discuss nonreciprocal thermal radiation. Moreover, the potential applications of nonreciprocity to other Laplacian physical fields are discussed. Finally, the prospects for advancing nonreciprocal thermal metamaterials are highlighted, including developments in device design and manufacturing techniques and machine learning-assisted material design.

Keywords: thermal metamaterials; nonreciprocity; nonlinearity; spatiotemporal modulation

1. Introduction

With the miniaturization of devices and chip integration in communication technology and electronic packaging, there is an increasing demand for materials with superior thermal properties. Based on the second law of thermodynamics, heat spontaneously flows from high temperature to low temperature in homogenous materials when a temperature gradient is present. This process of energy transfer is ubiquitous in nature. However, to guarantee the stability of the target system, manipulating the heat flux at will becomes a significant task. Because of the isotropic material parameters and fixed geometry shape, traditional thermal materials have a limited ability to tune thermal properties and adapt to complex heat flux distributions. Thus, it is urgent to examine novel thermal management methods. In this regard, thermal metamaterials inspired by electromagnetic metamaterials have attracted considerable attention to overcome the limitations of natural materials [1–2].

Metamaterials are artificially engineered media comprising a periodic or nonperiodic array of unit structures that demonstrate remarkable physical properties and applications such as electromagnetic invisibility cloaks [3–7], three-dimensional holograms [8], and achromatic metalens [9–10]. Previous studies on metamaterials were mainly focused on manipulating electromagnetic waves and investigated through the use of identical structural units arranged in a periodic layout to realize exotic physical phenomena such as negative refractive [11] and reversed Doppler effect [12]. Later, Pendry *et al* [4]. and Alù *et al* [13]. proposed transformation optics and scattering elimination theory, respectively, allowing metamaterials to control electromagnetic waves more effectively through the spatial sequence design of differentiated structural units. These metamaterial design approaches are not only applicable to wave fields (e.g., electromagnetic fields) but also to Laplace physical fields (e.g., thermal fields), which satisfy the second-order partial differential equation at the steady state $\nabla^2\varphi = 0$, where ∇^2 is the Laplacian operator and φ is the potential function, which can be a physical field, a combination of physical fields, or a nonlinear term of the original field T [14–15]. In 2008, Fan *et al.* [1] pioneered the concept of an electromagnetic invisibility cloak into the field of heat and theoretically predicted the thermal invisibility cloak. In 2012, Narayana *et al.* [16] proved by experiments the thermal invisibility cloak for the first time. Later, research on thermal invisibility cloaks has increased, and transient thermal invisibility cloaks and multifunction thermal invisibility cloaks have been explored successively [16–22]. With the proposal and implementation of the thermal invisibility cloak, several thermal metamaterials have emerged, including heat flow concentrators for collecting heat energy [17,23–25], heat flow rotators for rotating heat fields [16,26–27], thermal illusion devices for camouflage [28–31], and thermal encoding [32–33].

The abovementioned thermal metamaterials are reciprocal and present symmetry in energy transfer in opposite direc-

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tions. However, several scenarios require more precise and adaptive heat field regulation to overcome the inherent isotropic diffusion of heat flow and achieve directional control over both the magnitude and orientation of heat flux. Nonreciprocal thermal metamaterials provide a promising solution for achieving greater degrees of freedom in thermal field regulation, resulting in numerous novel applications. For example, researchers have proposed thermal diodes to allow unidirectional heat transfer [34], developed a geometric heat pump that pumps extra heat ably diffusing from cold to hot [35], and demonstrated a nonreciprocal infrared thermal emitter caused by a spatiotemporal modulation grating [36–38].

The design of nonreciprocal thermal metamaterials is mainly based on the Onsager reciprocity theorem. In this review, we offer a detailed introduction to this theory and examine many typical implementation methods, including nonlinearity, spatiotemporal modulation, and angular momentum bias, for realizing nonreciprocity in the thermal fields. Nonreciprocal thermal radiation using magnetic response, time-variant systems, and optical nonlinearity are also discussed. Finally, it outlooks several future directions for the development of nonreciprocal thermal metamaterials.

2. Onsager reciprocal relations

Reciprocity requires the system to exhibit symmetry in response to energy transfers that occur in opposite directions. Specifically, the transmission channel should respond symmetrically to the input source when the transmitter and receiver positions are interchanged. The notion of reciprocity was first discussed theoretically by Stokes and Helmholtz for light waves, followed by successive proposals of Lorentz reciprocity and Onsager reciprocity. Among these, the Onsager reciprocity can be applied to different irreversible physical processes such as acoustic, electromagnetic, mechanical, thermoelectric, and diffusion phenomena. In this section, we outline how the Onsager principle of microscopic reversibility is derived in a heat field.

At the microscopic level, most physical processes show time-reversal symmetry. On the basis of microscopic reversibility, Onsager explained the basic relationship between the time-reversal invariance of the microscopic dynamic equation and reciprocity. The Onsager reciprocity principle is derived from four fundamental assumptions [39]: time-reversal symmetry of microscopic equations, linearity, causality (an irreversible process that increases entropy), and thermodynamic quasiequilibrium (a system reaches a stable state after interacting with its surroundings for a sufficient amount of time).

Onsager reciprocity emphasizes that irreversible processes originate from a generalized flow J (the amount of heat flux and concentration passing through a unit area per unit time) driven by a generalized force X (temperature gradient, chemical potential gradient). In the thermal quasiequilibrium state, these two quantities follow a linear phenomenological relationship, denoted as Eq. (1).

$$J_i = \sum_j L_{ij} X_j \tag{1}$$

where L_{ij} refers to the phenomenological coefficient, indicating that the i-th generalized flow J_i is affected by the j-th generalized force X_j. Based on the limitation of the microscopic reversibility hypothesis, the linear phenomenological coefficients have symmetry of $L_{ij} = L_{ji}$, which is the Onsager reciprocity relation.

Specifically, for a three-dimensional anisotropic heat conduction process, the law of heat conduction (i.e., Fourier's law) can also be expressed in accordance with the phenomenological relationship of Eq. (2).

$$q_i = L_{ij} X_j, (i, j = x, y, z) \tag{2}$$

where q_i refers to the heat flux, and X_j refers to the temperature gradient. In Eq. (2), the phenomenological coefficient L_{ij} is the thermal conductivity as a tensor, with its value range in the Cartesian coordinate system (x, y, z) forming an ellipsoid characterized by three principal axes (a, b, c) of heat conduction. Based on the limitation of the linear assumption, the heat flux through any point on the surface of an object varies linearly with the temperature gradient. The phenomenological coefficients L_{ij} $(i, j = x, y, z)$ in the Cartesian coordinate system can be expressed as phenomenological coefficients M_{nn} $(n = a, b, c)$ along the principal axes, denoted as Eq. (3).

$$L_{ij} = \sum_{n=a,b,c} e_{in} e_{jn} M_{nn} = e_{ia} e_{ja} M_{aa} + e_{ib} e_{jb} M_{bb} + e_{ic} e_{jc} M_{cc} \tag{3}$$

where e_{ia}, e_{ja}, e_{ib}, e_{jb}, e_{ic}, and $e_{jc} (i,\ j = x, y, z)$ is the cosine of the angle between the Cartesian coordinate system and the direction corresponding to the principal axes. According to matrix arithmetic, the phenomenological coefficients L_{ij} in Eq. (3) is symmetric and can be a diagonalized matrix. Thus, the Onsager reciprocity is satisfied in the heat conduction process.

To realize nonreciprocity in a system, it is required to invalidate at least one of the four basic assumptions of Onsager reciprocity [39]. With regard to macroscopic heat conduction, causality is described by the second law of thermodynamics, which states that heat flows from high temperature to low temperature. This is a well-established law of nature and is hard to violate in everyday applications and most engineering systems. Albeit negative heat transfer phenomena have been achieved in certain extreme and specialized situations [1,16,27,40–41], the causality or the second law of thermodynamics is not violated essentially. For instance, by using a thermal rotator in a system with a fixed temperature difference, the local heat flux can be completely reversed. However, the heat flux still takes place from the high-temperature boundary to the low-temperature boundary from the angle of the whole system [27,40]. Thus, breaking causality in the overall heat transfer process is demanding.

Nonreciprocal heat transfer can be realized by using dissipative structures far from the distance equilibrium, which violates the thermodynamic quasiequilibrium assumption.

Dissipative structures are macroscopic structures that appear from the exchange of energy and matter between the system and its surroundings when the system is in a nonequilibrium state. The formation and maintenance of such structures are accompanied by dissipation. It was demonstrated that optical nonreciprocity and unidirectional energy transmission can be attained through system energy dissipation [42–43]. In heat conduction, the introduction of surface convection or radiant heat transfer allows the exchange of matter and energy with the surroundings [44]. This introduces nonlinear coupling and energy conversion into the heat transfer process, leading to a nonlinear relationship between the temperature gradient and heat flux, thus allowing nonreciprocal heat transfer. However, the principle of minimum entropy production ensures that the nonequilibrium state always converges to a fixed state within the system region over time, irrespective of external interference or internal parameter fluctuations. The disturbed dynamics will show higher entropy production than the original stationary state and eventually go back to its initial equilibrium [45]. Thus, thermodynamic quasiequilibrium is inherently stable, i.e., unbalanced processes naturally tend toward equilibrium.

In comparison to causality and thermodynamic quasiequilibrium, breaking the linear response and time-reversal symmetry makes it easier to realize nonreciprocal heat transfer, which has triggered immense attention in this area. In the following, a detailed discussion is presented regarding achieving thermal nonreciprocity according to these two assumptions. One approach is to use nonlinear thermal materials or structures in which physical transport properties are not constrained by the reciprocity theorem, which can break the linear response (Section 3.1). The second is to employ the speed generated by the linear spatiotemporal modulation (Section 3.2) or the angular momentum bias resulting from the rotation (Section 3.3), which can break the time-reversal symmetry.

3. Nonreciprocal thermal transfer

3.1. Nonreciprocal thermal transfer based on nonlinearity

The best way to realize thermal nonreciprocity using nonlinear thermal materials or structures lies in the realization of the nonlinearity of thermal conductivity. For passive conditions and without convection, the one-dimensional heat conduction equation is:

$$\rho c \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \quad (4)$$

where T refers to the temperature, x refers to the coordinates of the heat transfer direction, t refers to the time of heat transfer, κ refers to the thermal conductivity, and ρ and c refer to the density and specific heat capacity of the material, respectively. Generally, the thermal conductivity remains constant irrespective of temperature, thus making the governing equation a linear partial differential equation. As a consequence, Green's function can be utilized to solve the temperature distribution in heat conduction processes [46–48]. Based on the linear superposition principle, the field distribution of the heat source under the same boundary conditions can be acquired using Green's function (field generated by the point heat source). In this case, Green's function is symmetric, i.e., the field is symmetric with respect to the source [49]. Thus, the heat conduction process satisfies the reciprocity theorem on both local and global scales [50]. However, if the thermal conductivity of the material is temperature-dependent, the governing equation transforms into a nonlinear partial differential equation:

$$\rho c \frac{\partial T}{\partial t} = \kappa(T) \frac{\partial^2 T}{\partial x^2} \quad (5)$$

Consequently, obtaining a solution via Green's function becomes unattainable and makes the reciprocity relation invalid.

To realize a nonreciprocal heat conduction process, nonlinear thermal materials with temperature-dependent thermal conductivity can be employed. Considering nonlinear isotropic thermal materials 1 and 2, material 1 demonstrates a positive correlation between thermal conductivity and temperature, while material 2 has a negative correlation (the top left of Fig. 1(a)). First, the nonreciprocity of heat conduction can be attained using a single nonlinear thermal material 1 combined with the asymmetry of space geometry. Because more parts of the system can be heated from the right side, when the heat source and cold source are exchanged, the amount of heat in the forward direction should be small compared with that in the backward direction. Therefore, the heat conduction process in the two directions is nonreciprocal and is confirmed (the bottom left of Fig. 1(a)). From this phenomenon, this structure can be utilized as a thermal diode [51] or a thermal rectifier [52]. However, the thermal rectification ratio ($\eta = |Q(-\Delta T)|/|Q(\Delta T)|$ (where $|Q(\Delta T)|$ and $|Q(-\Delta T)|$ denote the heat fluxes in the forward and backward directions, respectively) of the structure is as low as 100.48% when ΔT = 25 K, leading to suboptimal performance as a thermal diode or rectifier. To further enhance the thermal rectification ratio, asymmetric nonlinearity is proposed as a possible method by simultaneously utilizing nonlinear thermal materials 1 and 2 (the bottom right of Fig. 1(a)). The heat flux through the asymmetric geometry and asymmetric nonlinearity system is displayed in the upper right corner of Fig. 1(a). Due to the contrasting temperature dependence of materials 1 and 2, both regions show high (low) thermal conductivity concurrently during forward (backward) heat conduction, giving rise to an outstandingly high thermal rectification ratio of up to 184.32% at ΔT = 25 K. These results imply that realizing thermal rectification in one-dimensional thermal diffusion requires the inseparability of spatial and temperature-dependent thermal conductivities [53].

Besides using nonlinear thermal materials directly, a structure with a specific response to temperature can also be used to attain the nonlinear equivalent thermal conductivity of the system. For instance, a macroscopic thermal diode can

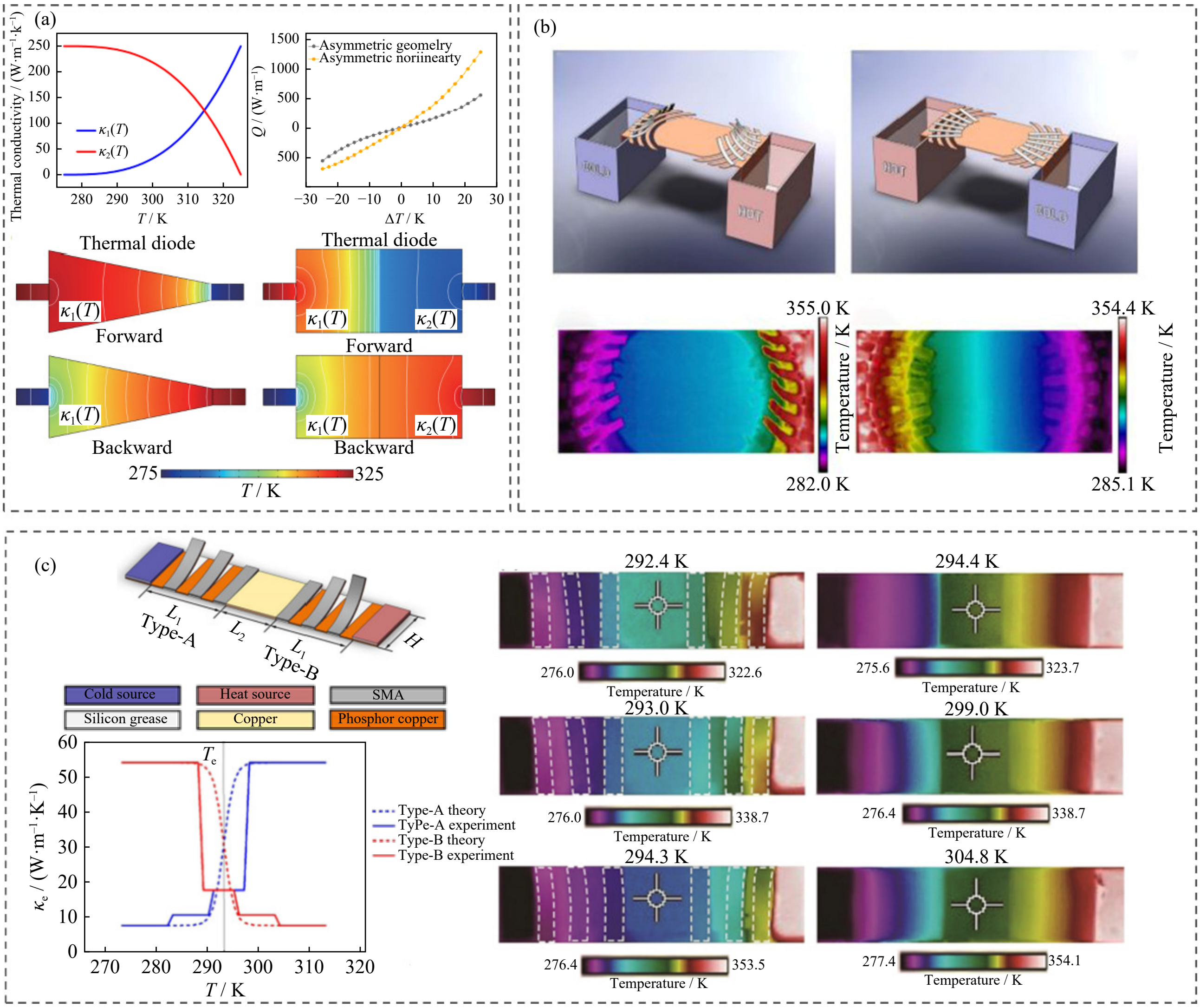

Fig. 1. Nonreciprocity resulting from nonlinear thermal materials: (a) thermal diode made of nonlinear material. Two nonlinear materials (top left), steady-state temperature distribution in geometric asymmetry composed of material 1 (bottom left) and geometric symmetry structure spliced by materials 1 and 2 (bottom right), and heat flow across the two systems (top right). Reprinted figure with permission from [50] as follows: Y. Li, J.X. Li, M.H. Qi, C.W. Qiu, and H.S. Chen, *Phys. Rev. B*, 103, 014307 (2021). Copyright 2021 by the American Physical Society; (b) nonlinear structure-based macroscopic thermal diode. Diode in the off-state (first column) or on-state (second column). Reprinted figure with permission from [54] as follows: Y. Li, X. Shen, Z. Wu, *et al*., *Phys. Rev. Lett.*, 115, 195503 (2015). Copyright 2015 by the American Physical Society; (c) isolation thermostat constructed with a nonlinear structure. Left: structure of the isolation thermostat and material properties of two shape memory alloys; right: effect of the isolation thermostat structure at different heat source temperatures. Reprinted figure with permission from [55] as follows: X. Shen, Y. Li, C. Jiang, and J. Huang, *Phys. Rev. Lett.*, 117, 055501 (2016). Copyright 2016 by the American Physical Society.

be fabricated with shape memory alloys that deform with temperature (Fig. 1(b)) [54]. The left-hand alloy demonstrates flattening behavior at high temperatures and bending behavior at low temperatures, whereas the right-hand alloy has flattening behavior at low temperatures and bending behavior at high temperatures. Temperature-dependent variations in alloy shape indirectly affect the equivalent thermal conductivity of the system. When the left container (blue) is filled with cold water and the right container (red) is filled with hot water, both shape memory alloys simultaneously experience warping (the top left of Fig. 1(b)). During this process, the system shows an extremely low equivalent thermal conductivity, inhibiting heat transfer from the heat source to the cold one, leading to an off-state for the diode (the bottom left of Fig. 1(b)). However, switching the locations of the two containers, both shape memory alloys are straight (the top right of Fig. 1(b)). At this stage, there is a significantly high effective thermal conductivity within the system, facilitating heat flow throughout and giving rise to an on-state for the diode (the bottom right of Fig. 1(b)).

Similarly, sandwich structures of isolation thermostats can be realized using shape memory alloys (SMA) to achieve nonreciprocal isolation protection [55–56]. In the top left of Fig. 1(c), the middle section (light yellow) comprises copper, whereas the terminals are composed of distinct shape memory alloys (gray) and phosphor copper (orange) with identical phase transition temperatures but opposite phase transition characteristics: Type-A flattens at high temperature and bends at low temperature, whereas Type-B has the opposite behavior. The effective thermal conductivities of Type-A and Type-B as a function of temperature are shown at the bottom of Fig. 1(c). When connected to the heat source and the cold source, both shape memory alloys simultaneously experience warping, leading to a simultaneous decrease in effective thermal conductivity at both ends and forming an isolated protection effect in the middle region (as shown in the right panel of Fig. 1(c)). The central temperature of the experimental group remains relatively stable compared with that of the control group. In addition, the nonlinear heat transfer process can be constructed by using the variation of thermal conductivity with ambient temperature during phase transformation processes, such as solid–liquid phase transition [57] and liquid–solid composites [58].

3.2. Nonreciprocal thermal transfer based on spatiotemporal modulation

Because the thermal conductivity of nonlinear thermal materials depends on temperature, the constructed thermal nonreciprocal devices are limited to specific operating temperatures. To overcome this limitation, a spatiotemporal medium is introduced, which breaks the symmetry of temporal and spatial inversion in linear systems, allowing the realization of thermal nonreciprocity.

Without convection and under passive conditions, nonreciprocal heat transport can be achieved by introducing traveling-wave spatiotemporal modulation (resembling a traveling wave-like change over time and space) in both volumetric heat capacity (the product of mass density ρ and specific heat capacity c) and thermal conductivity. In this scenario, the one-dimensional heat conduction equation can be reformulated as

$$C(x-v_0t)\frac{\partial T}{\partial t}=\frac{\partial}{\partial x}\left[\kappa(x-v_0t)\frac{\partial T}{\partial x}\right] \tag{6}$$

where $C(x-v_0t)$ refers to the volumetric heat capacity and $\kappa(x-v_0t)$ denotes the thermal conductivity. Considering a simple modulation case for these two parameters,

$$C(x-v_0t)=C_0[1+\Delta C\cos(\beta(x-v_0t))] \tag{7}$$

$$\kappa(x-v_0t)=\kappa_0[1+\Delta\kappa\cos(\beta(x-v_0t)+\delta)] \tag{8}$$

Both demonstrate periodic variations between the minimum value ($C_0(1-\Delta\rho)$, $\kappa_0(1-\Delta\kappa)$) and the maximum value ($C_0(1+\Delta\rho)$, $\kappa_0(1+\Delta\kappa)$), where β is the wavenumber, v_0 is the speed of movement, C_0 and κ_0 are the volumetric heat capacity and thermal conductivity of the initial homogeneous material, respectively, and ΔC and $\Delta\kappa$ are their modulation amplitudes.

The modulation of volumetric heat capacity encompasses two distinct scenarios: one is the modulation of mass density, and the other is the modulation of heat capacity. In continuous media, mass conservation is maintained by the continuity equation $\partial\rho/\partial t+\nabla\cdot(\rho v_0)=0$, incorporating an additional convection term of $\nabla\cdot(CTv_0)$ that is not included in Eq. (6). Therefore, without an external energy or mass input, a physical system keeps a constant mass density over time as governed by the principle of mass conservation [59]. Thus, rather than relying on density modulation, a tunable specific heat capacity can serve as a viable alternative since the product of density and heat capacity is what ultimately matters.

According to Bloch's theorem, the temperature distribution of heat wave diffusion is

$$T=\phi(x-v_0t)\mathrm{e}^{i(\beta x-\omega t)} \tag{9}$$

where β and ω are the wavenumber and frequency, respectively, and $\phi(x-v_0t)$ is an amplitude-modulated function that shares the same period as $C(x-v_0t)$ and $\kappa(x-v_0t)$ in Eq. (6).

By substituting Eqs. (7)–(9) into Eq. (6) and adopting the homogenization theory of differential equations [60], we can obtain the homogeneous equation with a constant coefficient that has the same solution as Eq. (6) [61–62]:

$$C^*\frac{\partial\tilde{T}}{\partial t}+V\frac{\partial\tilde{T}}{\partial x}-\kappa^*\frac{\partial^2\tilde{T}}{\partial x^2}-S\frac{\partial^2\tilde{T}}{\partial x\partial t}=0 \tag{10}$$

Compared with the one-dimensional diffusion equation, the spatiotemporal modulated thermal diffusion equation has two terms: the convection-like term $V\frac{\partial\tilde{T}}{\partial x}$ and the thermal equivalent term $S\frac{\partial^2\tilde{T}}{\partial x\partial t}$ (to be discussed below). The convection-like term ($V\frac{\partial\tilde{T}}{\partial x}$) can break the spatial inversion symmetry, facilitating the realization of nonreciprocal thermal diffusion. The appearance of this convection-like term represents the effect of "medium bias" due to the spatial modulation of the parameters. Thus, the spatial direction preference of thermal diffusion will emerge [63]. Both the convection-like and convection terms can achieve nonreciprocal heat transfer. Compared with convection terms involving actual mechanical or physical flow [64–65], the convection-like term resulting in nonreciprocal heat transfer includes only the "motion" of material parameters. The homogenization parameters in Eq. (10) are described as follows:

$$\kappa^*\approx\kappa_0\left[1-\frac{(\Delta\kappa)^2}{2}\frac{1}{1+\Gamma^2}\right] \tag{11}$$

$$C^*\approx C_0\left[1-\frac{(\Delta C)^2}{2}\frac{\Gamma^2}{1+\Gamma^2}\right] \tag{12}$$

$$V\approx v_0\kappa_0\beta\frac{\Delta C\Delta\kappa}{2}\frac{1}{1+\Gamma^2}(\cos\delta+\Gamma\sin\delta) \tag{13}$$

$$S\approx\frac{1}{v_0}C_0\frac{\Delta C\Delta\kappa}{2\beta}\frac{\Gamma^2}{1+\Gamma^2}(\cos\delta+\Gamma^{-1}\sin\delta) \tag{14}$$

where $\Gamma=v_0C_0/\beta\kappa_0$ denotes the dimensionless modulation speed and $\tilde{T}$ refers to the envelope of the actual temperature wave.

When the modulation speed $\Gamma=0$, the homogenization parameters V and S are both zero, and the homogenization material parameters show that the average volumetric heat capacity $C^*=C_0$ and the equivalent thermal conductivity $\kappa^*=\kappa_0\left[1-(\Delta\kappa)^2\right]$, leading to reciprocal thermal diffusion. Similarly, reciprocal thermal diffusion can also be realized by setting the modulation speed $\Gamma\to+\infty$ where homogenization parameters V and S approach zero and the homogenization material parameters show equivalent volumetric heat capacity $C^* = C_0\left[1-(\Delta C)^2\right]$ and average thermal conductivity $\kappa^* = \kappa_0$. However, when the modulation speed $\Gamma \neq 0$, a nonzero value of V will introduce a convective term, leading to a biased temperature distribution that exhibits nonreciprocity of thermal diffusion, as displayed in Fig. 2(a) [66].

It is clear that both C^* and κ^* are independent of the phase difference δ in Eqs. (11)–(14), while parameters V and S show dependence on the phase difference δ. The phase difference δ provides a flexible and tunable parameter to control the degree of nonreciprocity by affecting V and S. By manipulating the position of the heat source and the modulation direction of the parameters, the direction of heat flow transmission can possibly be controlled, as illustrated in Fig. 2(b) [62]. When keeping a fixed position for the heat source, modifying the direction of parameter modulation leads to a corresponding reversal in the direction of heat flow transmission. Conversely, if we exchange the position of the heat source while keeping the direction of parameter modulation unchanged, the opposite effect is observed in heat flow transmission. To depict the effect of phase difference δ on the degree of nonreciprocity, the forward and backward-1 cases (Fig. 2(b)) with the same modulation direction but opposite source position are taken as examples. When $\delta = -\pi/4$, the evolution of temperature and heat flux (the first column of Fig. 2(c)) for these two cases is the same, demonstrating reciprocal propagation. Meanwhile, when $\delta = \pi/4$, the temperature amplitudes and heat flux are different, demonstrating nonreciprocal propagation (the second column of Fig. 2(c)).

In Eq. (10), we find that the homogenization equation has an additional term of $S\dfrac{\partial^2\tilde{T}}{\partial x\partial t}$, which is the thermal equivalent term of the Willis coefficient in the elastic dynamics of an inhomogeneous medium [67]. Thermal Willis coupling in thermal diffusion is the interplay between heat flux and temperature change rate. The time-independent convection-like term ($V(\partial\tilde{T}/\partial x)$) can break the spatial inversion symmetry and realize asymmetric diffusion in both transient and quasisteady states. While the thermal equivalent term ($S\dfrac{\partial^2\tilde{T}}{\partial x\partial t}$) is

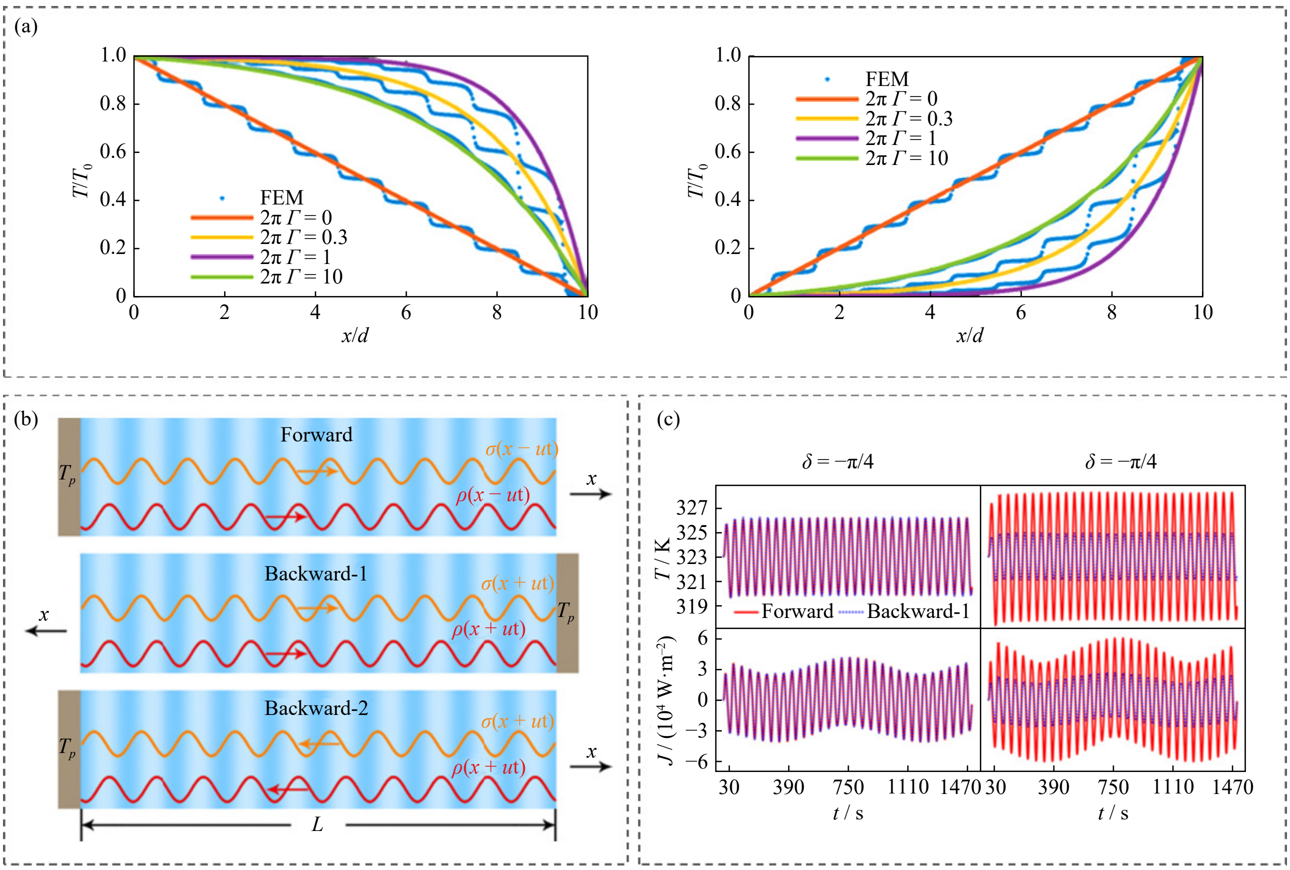

Fig. 2. Nonreciprocal thermal diffusion in spatiotemporal modulated materials: (a) nonreciprocal temperature distributions in spatiotemporal modulated metamaterials under forward (left) and backward (right) propagation. Γ is the space–time modulation moving speed. $\Gamma = 0$ denotes no modulation. The nonreciprocal effect shows an initial increase and then a decrease as the modulation speed varies. Reprinted figure with permission from [66] as follows: D. Torrent, O. Poncelet, and J.C. Batsale, *Phys. Rev. Lett.*, 120, 125501 (2018). Copyright 2018 by the American Physical Society; (b) forward propagation of temperature waves in metamaterials (top) and two backward propagation scenarios: changing the source position but maintaining the modulation direction (middle) and changing the modulation direction but maintaining the source position (bottom). u is modulation speed and equivalent to the speed of movement v_0; (c) phase difference δ measures the extent of nonreciprocity. When $\delta = -\pi/4$, nonreciprocity disappears, and when $\delta = \pi/4$, heat wave propagation shows nonreciprocal behavior. Reprinted figure with permission from [62] as follows: L.J. Xu, J.P. Huang, and X.P. Ouyang, *Phys. Rev. E*, 103, 032128 (2021). Copyright 2021 by the American Physical Society.

time-dependent and relies on the rate of temperature change, nonreciprocal thermal diffusion by Willis coupling takes place only in transient processes [63,68].

A Willis thermal metamaterial, developed with spatiotemporal modulation, has precise control over the directional propagation of the temperature field. Its propagation direction can be reversed precisely around the critical point of the modulation speed (Fig. 3(a)) [69]. In porous media, the Fizeau drag in thermal diffusion can be observed in the Willis thermal metamaterial (Fig. 3(b)), indicating distinct propagation velocities of the temperature field in opposite directions and giving rise to a nonreciprocal process of thermal diffusion [70]. The spatiotemporal modulation-based Willis coupling not only realizes nonreciprocal thermal diffusion but also offers ideas for controlling nonequilibrium mass and energy transport.

The material's thermal parameters with wave-like modulation that achieve a nonreciprocal heat transfer process can be determined by switching between low and high thermal conductivity and heat capacity states. When material parameters present sensitivity to external stimuli (such as magnetic fields, electric fields, and light), periodically arranged layered media can be produced by applying periodic external stimuli. For example, upon exposure to ultraviolet (375 nm) and green light (530 nm), the azobenzene polymer shows a rapid reversal of thermal conductivity at room temperature within seconds [71]. The layered structure, comprising *p*-azobenzene polymer layers, uses ultraviolet and green period-lighting to efficiently modulate thermal conductivity and volumetric heat capacity. On the basis of this method, a thermal diode with a rectification factor ($R = \frac{||Q_F(x=d)|-|Q_B(x=0)||}{\max[|Q_F(x=d)|;|Q_B(x=0)|]}$, where $Q_F(x=d)$ and $Q_B(x=0)$ are the forward and backward heat fluxes at $x=d$ and $x=0$, respectively) above 86% has been attained (Fig. 3(c)) [68]. Compared with traditional nonlinear steady-state diodes, this diode is implemented by propagating heat waves driven by Willis coupling produced through spatiotemporal modulation of thermal parameters.

3.3. Nonreciprocal thermal transfer based on angular momentum

Another way to realize nonreciprocity in linear systems is based on the Zeeman effect caused by angular momentum bias. For example, in a three-port annular cavity with rotating airflow, the circular motion of the airflow induces an angular momentum bias that results in the acoustic Zeeman effect, thereby allowing nonreciprocal acoustic behavior of the device [72]. In convection–diffusion systems, the Zeeman effect originates from the angular momentum bias induced by the volume force that acts on the fluid, which can be gravity, centrifugal force, or other forms of force [73].

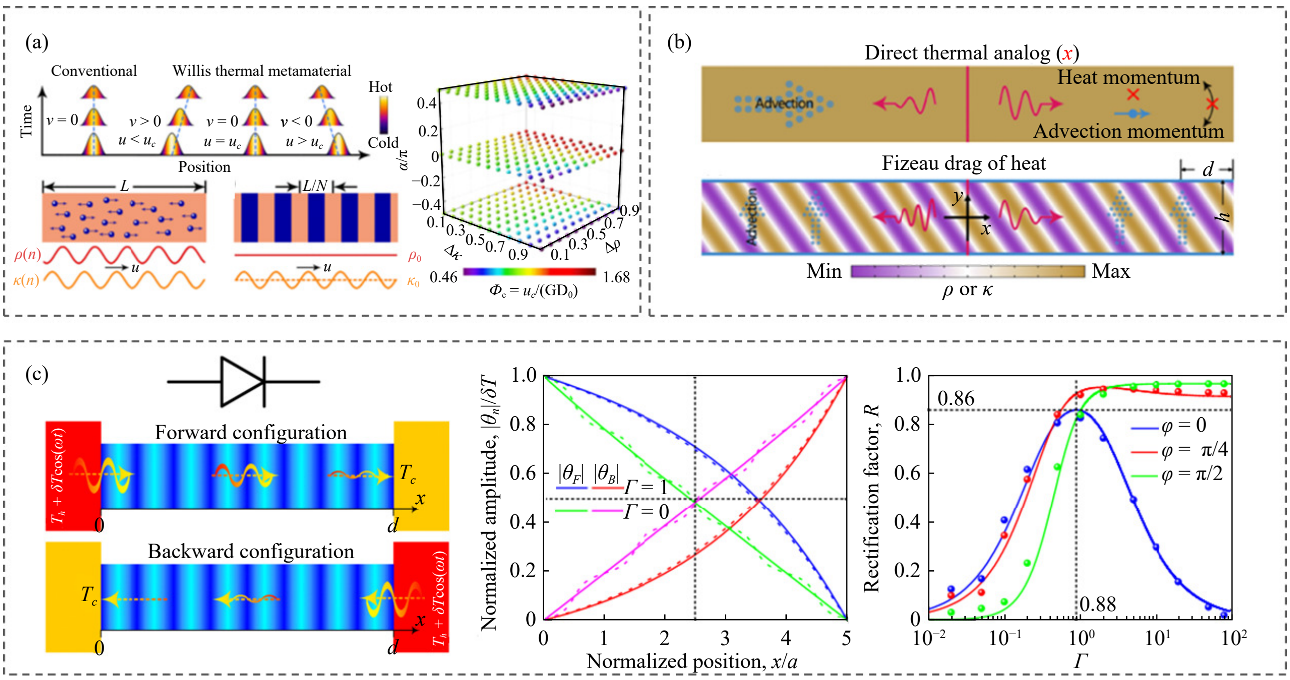

Fig. 3. Spatiotemporally modulated nonreciprocal thermal metamaterials: (a) asymmetric thermal diffusion in Willis thermal metamaterials induced by spatiotemporal modulation parameters. Reprinted figure with permission from [69] as follows: L.J. Xu, G.Q. Xu, J.X. Li, Y. Li, J.P. Huang, and C.W. Qiu, *Phys. Rev. Lett.*, 129, 155901 (2022). Copyright 2022 by the American Physical Society; (b) thermal Fizeau drag resulting from the thermal Willis coupling mechanism. Reprinted figure with permission from [70] as follows: L.J. Xu, G.Q. Xu, J.P. Huang, and C.W. Qiu, *Phys. Rev. Lett.*, 128, 145901 (2022). Copyright 2022 by the American Physical Society; (c) thermal wave diodes show rectification of the heat flux in forward and backward propagation (left). The amplitude profiles of the temperature field are shown in the center, and the right panel displays the rectification coefficient. The arrows and their amplitudes are the direction and magnitude of the heat wave, respectively. Reprinted figure with permission from [68] as follows: J. Ordonez-Miranda, Y.Y. Guo, J.J. Alvarado-Gil, S. Volz, and M. Nomura, *Phys. Rev. Appl.*, 16, L041002 (2021). Copyright 2021 by the American Physical Society.

In a one-dimensional scenario with convection velocity v, the diffusion equation is

$$\rho c\frac{\partial T}{\partial t}=\kappa\frac{\partial^2 T}{\partial x^2}-\rho c v\frac{\partial T}{\partial x} \quad (15)$$

where ρ, c, κ, and v are the temperature-independent mass density, specific heat capacity, thermal conductivity, and convective velocity of the fluid, respectively. Fluid refers to a steady, incompressible creeping flow between parallel plates, with its velocity demonstrating a parabolic distribution along the vertical direction of the flow. For a narrow plate of height$h$, the convective velocity is represented by $v=-h^2(\nabla P-f)/(12\mu)$, where μ is the dynamic viscosity, P is the pressure, and f is the volume force applied to the fluid. As shown on the left side of Fig. 4(a), the fluid velocity $+v_0(-v_0)$ is produced by the fluid pressure in the $+x(-x)$ direction. The application of a volume force f to the fluid induces an additional convective velocity in the direction of the force. The fluid velocity in the $+x(-x)$ direction is $v_+(v_-)$, while $|v_+|\neq|v_-|$.

By applying a periodic temperature input aligned with the fluid flow direction $T=T_0+A\cos(\beta x-\omega t)$, where T_0, A, β, and ω are the reference temperature, temperature amplitude, wavenumber, and frequency, respectively. By taking the counterclockwise direction as the $+x$ direction (indicated by the blue arrow in Fig. 4(a)) and substituting the periodic temperature into the convection–diffusion equation, a frequency

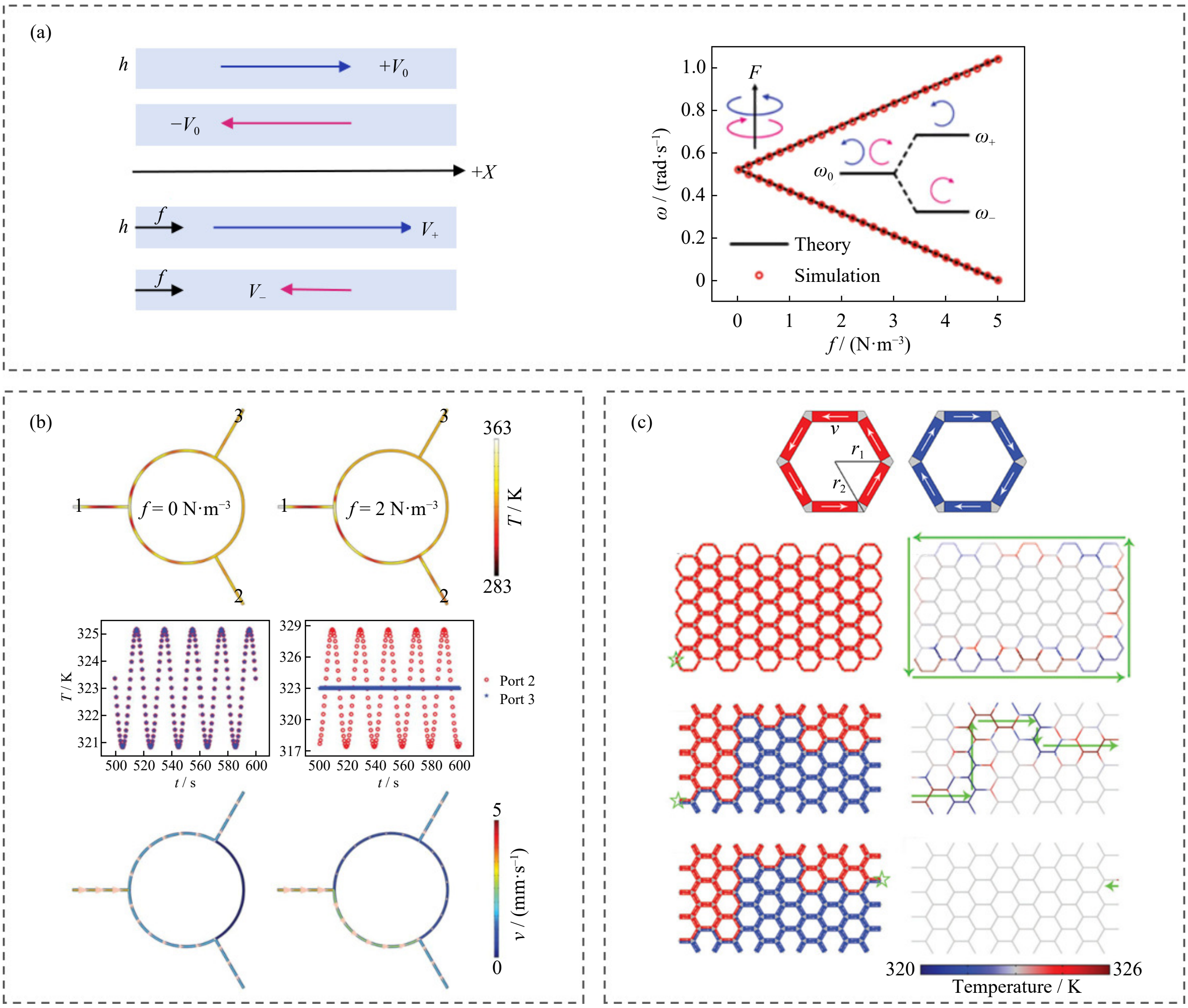

Fig. 4. Thermal nonreciprocity induced by angular momentum bias: (a) thermal Zeeman effect. Schematic of the frequency splitting principle (left) and degree of splitting of the real part of the frequency as a function of the volume force (right); (b) nonreciprocal heat transport due to the thermal Zeeman effect. An angular momentum bias ring exhibiting thermal nonreciprocity and isolation in which the fluid is water. Temperature distribution at 600 s under different volume forces (first row), temperature changes at ports 2 and 3 under different volume forces for 500 to 600 s (second row), and convective velocity distribution (third row). Reprinted with permission from L.J. Xu, J.P. Huang, and X.P. Ouyang, *Appl. Phys. Lett.*, 118, 221902 (2021) [73]. Copyright 2021 AIP Publishing LLC; (c) topological protection in thermal convection–diffusion systems. Two thermal spin structures (first row) consisting of counterclockwise (red unit) and clockwise convection (blue unit), topological protection in the unidirectional hot edge state (second line), and unidirectional heat transfer at the topological thermal interface state (third and fourth lines). Reprinted from L.J. Xu and J.P. Huang, *EPL Europhys. Lett.*, 134, 60001 (2021) [75]. © IOP Publishing. Reproduced with permission. All rights reserved.

of $\omega_0 = \beta v_0 - \mathrm{i}\beta^2 D$ with the thermal diffusion coefficient $D = \kappa/(\rho c)$ is obtained for both clockwise and counterclockwise directions when no volume force exists. $\mathrm{Re}(\omega_0)$ and $-\mathrm{Im}(\omega_0)$ are the frequency and attenuation factor of temperature waves during propagation, respectively [74].

If volume force $f = 0$, the counterclockwise and clockwise frequencies are no longer equal and can be mathematically expressed as follows:

$$\omega_{\pm} = \beta v_{\pm} - \mathrm{i}\beta^2 D \quad (16)$$

where convective velocities $v_{\pm} = v_0 \pm h^2 f/(12\mu)$. This phenomenon of frequency splitting caused by the angular momentum bias created by the volume force is called the thermal Zeeman effect, and the degree of frequency splitting increases with increasing volume force (the right picture in Fig. 4(a)).

In Fig. 4(b), Xu *et al.* [73] demonstrated nonreciprocal heat transport due to the thermal Zeeman effect in a fluid-filled three-port ring cavity. The fluid flow within the cavity can be considered as the flow between the narrow plates. Port 1 acts as the input port (high voltage P_H), while ports 2 and 3 are output ports (low voltage P_L). A periodic temperature source is placed on port 1, with ports 2 and 3 set as open borders. For zero-volume forces, the ring exhibits two symmetric velocities ($v_{1\to2} = v_{1\to3}$) with identical temperature amplitudes at ports 2 and 3. When a counterclockwise volume force is applied, $v_{1\to2}$ increases while port $v_{1\to3}$ decreases, leading to an increase in temperature amplitude at port 2 and complete temperature isolation at port 3, which achieves the nonreciprocal propagation of heat waves and the temperature isolation of port 3. The utilization of thermal nonreciprocity caused by angular momentum bias can be utilized to realize topological protection [75], as depicted in Fig. 4(c). A thermal spin structure with counterclockwise or concurrent flow is arranged in a honeycomb lattice. When the heat source is positioned in the lower left corner, a unidirectional thermal edge state appears within the lattice [76]. This phenomenon arises because of the nonreciprocal thermal isolation induced by the angular momentum bias resulting from the spin of the fluid in the structure, allowing the lattice surface to only support temperature propagation in the same direction as the spin of the structural unit (the second row of Fig. 4(c)). Combining two types of thermal spin structures results in the formation of topological interface states at their interface [77]. Because of the distinct convection directions of the two thermal spin unit structures, the attenuation rate is minimized at the unique boundary surface with a matching convection direction. This allows the heat wave to propagate along the flow field while preventing its propagation along the countercurrent field, thus realizing nonreciprocal propagation of the heat wave (the third and fourth lines of Fig. 4(c)) [75]. The results presented here provide potential for examining the topological properties related to diffusion dynamics, in particular those related to topological heat.

4. Nonreciprocal thermal radiation

Besides the above nonreciprocal thermal transfer, recently, nonreciprocal thermal radiation is also a rapid development direction for nonreciprocal thermal metamaterials.

Thermal radiation processes are governed by Kirchhoff's law [78]:

$$e(\omega, \theta, \phi) = \alpha(\omega, \theta, \phi) \quad (17)$$

where e and α refer to the directional spectral emissivity and absorptivity, respectively, ω refers to the frequency, and ϕ and θ refer to the azimuth angle and pitch angle, respectively. From Eq. (17), the structures or devices with high/low absorption also have high/low emission characteristics, which limits the energy conversion efficiency in solar energy harvesting [79] and radiative cooling [80]. Thus, researchers are striving to overcome this balance limitation to realize nonreciprocal emission/absorption.

The essence of the thermal radiation process is that an object with a temperature above absolute zero radiates electromagnetic waves outward. This phenomenon follows the Lorentz reciprocity theorem, which acts as a case of the application of the Onsager reciprocal relations to electromagnetic processes [39]. Kirchhoff's law, in accordance with the Lorentz reciprocity theorem, is applicable only to nonmagnetic, time-invariant, and linear materials. As a consequence, it becomes feasible to realize nonreciprocal emission and absorption by removing any of the three conditions, such as magnetic response, time-variant systems, or optical nonlinearity [81].

4.1. Nonreciprocal thermal radiation dependent on the magnetic response

One approach to breaking the Lorentz reciprocity is to utilize materials with an asymmetric permittivity tensor. For example, under an external magnetic field, the permittivity of a magneto-optical material is characterized by an asymmetric tensor. Among these materials, InAs, which is a prominent magneto-optical material, has been extensively applied to achieve heightened nonreciprocity. For example, Zhu *et al.* [78] first proposed a grating structure madding of InAs to show the violation of Kirchhoff's law. The one-dimensional grating of n-InAs atop aluminum is shown at the top of Fig. 5(a). Under external magnetic field $B = 3T$ in the z-direction, the absorptivity and emissivity no longer overlap, and Kirchhoff's law of thermal radiation is almost completely broken (the bottom of Fig. 5(a)). Later, many structures based on InAs with different physical mechanisms have been introduced into thermal emitters to achieve strong nonreciprocal radiation [82–85].

However, the utilization of nonreciprocal thermal emitters fabricated from InAs is typically confined to a large applied magnetic field, which restricts its potential applications. Without an external magnetic field, magnetic Weyl semimetals (WSMs) can violate Lorentz reciprocity and time-reversal symmetry, which is due to the significant anomalous Hall effect, which is linked to an improved Berry curvature at the Weyl nodes [86]. The vector 2b that separates the two Weyl cones in momentum space functions similarly to an internal magnetic field, as shown at the top of Fig. 5(b). WSM-

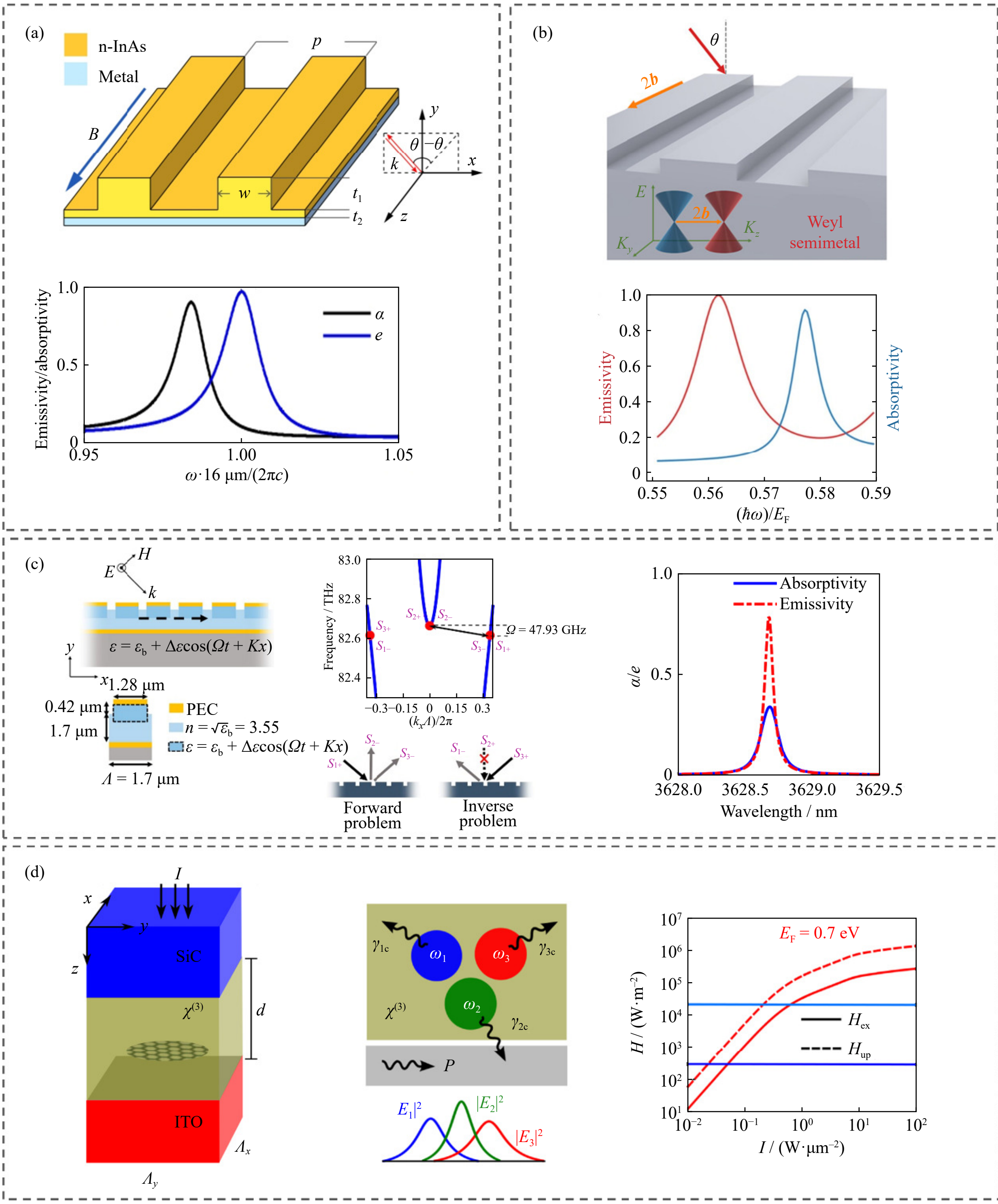

Fig. 5. Nonreciprocal thermal radiation in different mechanisms: (a) grating of n-InAs atop aluminum (top). The structure is periodic in the x direction, and has the following geometry parameters: p = 7.24 μm, w = 3.2 μm, t_1 = 1.981 μm, and t_2 = 0.485 μm. Emissivity spectra (e) and absorptivity spectra (α) at θ = 162.8° (bottom). Reprinted figure with permission from [78] as follows: L.X. Zhu and S.H. Fan, *Phys. Rev. B*, 90, 220301 (2014). Copyright 2014 by the American Physical Society; (b) Weyl semimetallic photonic crystals for nonreciprocal thermal emission(top). Emissivity and absorptivity spectra in the θ = 80° direction [86]. Reprinted with permission from B. Zhao, C. Guo, C.A.C. Garcia, P. Narang, and S. Fan, *Nano Lett*., 20, 1923 (2020) [86]. Copyright 2020 American Chemical Society; (c) grating design and the corresponding unit cell (left) with period Λ = 1.7 μm. The dashed region undergoes a time-dependent modulation of the refractive index. Band structure of grating (middle) and unequal absorptivity and emissivity (right). Reprinted with permission from A. Ghanekar, J.H. Wang, S.H. Fan, and M.L. Povinelli, *ACS Photonics*, 9, 1157 (2022) [37]. Copyright 2022 American Chemical Society; (d) nonreciprocal thermal radiation based on Kerr nonlinearity. Schematic of the three resonators at equal temperature supporting modes (middle). Heat extraction power H_{ex} from the emitter and unconverted power H_{up} compared with the temperature-driven radiative heat transfer between two vacuum-separated SiC plates held at 300 K (light blue) and 1 K (dark blue) temperature differences [108].

based emitters can break Kirchhoff's law of thermal radiation even without a magnetic field (the bottom of Fig. 5(b)). Over the past few years, many photonic structures involving magnetic Weyl semimetals, including one-dimensional nanowire arrays [87] and planar structures [88–89], have been developed to breach the reciprocity between absorbance and emittance.

The above structures rely on the external/internal magnetic response and can be summarized as grating structures [82–87,90–92], thin film structures [89,93], and multilayer structures [94–100], which refer to a number of physical effects, including guided mode resonance, surface plasmon resonance, Tamm plasmon resonance, Fabry–Perot resonance, topological interface state, and bound state in the continuum. Very recently, it is heartening to note that the experimental demonstration of strong nonreciprocal radiation has been realized [101–103].

4.2. Nonreciprocal thermal radiation in time-variant systems

Time modulation provides a magnet-free alternative to breaking the Lorentz reciprocity [37–38]. Nonreciprocal emission and absorption based on time-variant systems have been experimentally demonstrated at radio frequencies [104], demonstrating the potential of spatiotemporal modulation methods for thermal management and energy harvesting at infrared frequencies. The left view of Fig. 5(c) presents a nonreciprocal infrared thermal emitter that depends on dynamic modulation using the spatiotemporal grating refractive index to drive photon transitions between guided resonance modes [37]. It includes a dielectric grating coated with a perfect electrical conductor on both the top and bottom surfaces, and a detail of the unit cell is shown below the grating. The region marked by the dashed line undergoes a spatiotemporal permittivity modulation represented by $\varepsilon = \varepsilon_b + \Delta\varepsilon\cos(\Omega t + Kx)$, where ε_b refers to the base permittivity of the dielectric, $\Delta\varepsilon$ refers to the amplitude of modulation, Ω refers to the modulation frequency, and K refers to the spatial frequency of modulation. $\tau = \Delta\varepsilon/\varepsilon_b$ is the modulation depth. For zero modulation depth, the band structure of the grating plots is in the middle of Fig. 5(c). Modes excited by S_{1+} and S_{2+} are separated by modulation frequency Ω = 47.93 GHz and normalized wave vector $K\Lambda/2\pi = \pm 1/3$. The forward (modes excited by obliquely incident wave S_{1+} can couple to outgoing waves S_{2-} and S_{3-}) and inverse (an outgoing wave S_{1-} can result only from input wave S_{3+}) problems are defined. This demonstrates that the grating exhibits perfect nonreciprocal reflection (the right of Fig. 5(c)). It turns out that the time modulation of the Fermi energy of graphene can be used to generate nonreciprocity [38]. These works offer an idea for the development of nonreciprocal thermal emitters using electro-optical devices. Time modulation can also be employed to achieve photon refrigeration [105] and heat radiation pumps [106–107].

4.3. Nonreciprocal thermal radiation using a nonlinear material

The violation of Lorentz reciprocity can take place in nonlinear materials, as exemplified by the Kerr effect used in thermal radiation control [108–109]. The Kerr effect, a typical nonlinear optical effect, originates from the three-boundary nonlinear coefficients of materials. When an intense laser beam impinges on a material, changes in its refractive index occur, which in turn influences the transmission characteristics of the laser.

As shown in the middle of Fig. 5(d), a three-resonator system is considered [108], involving resonators that support modes at ω_1, ω_3, and the resonator with resonant frequency $\omega_2 = (\omega_3 - \omega_1)/2$ is excited by laser irradiance and placed in a nonlinear material with $\chi^{(3)}$ nonlinearity. Through a four-wave mixing process, photons in resonators 1 and 3 are coupled through interaction with excited photons in resonator 2. In such a four-wave mixing process, the total photon number is conserved, and the coupling between resonance modes 1 and 3 is nonreciprocal. The physical construction of such a scheme involves an indium tin oxide absorber (resonator 3) and a silicon carbide (SiC) emitter (resonator 1), with a nonlinear $\chi^{(3)}$ spacer in between (the left of Fig. 5(d)). Graphene nanosheets with fermi energy E_F = 0.7 eV are employed to produce strong local plasmon resonances to improve the nonlinear response. Calculations based on coupled-mode theory show that heat is extracted from the SiC emitter (the right of Fig. 5(d)) even when the two substrates are at the same temperature. The heat extraction study confirmed the significant potential of refrigeration using Kerr nonlinearity.

5. Nonreciprocity in other Laplace fields

In the earlier sections, we extensively examined nonreciprocity phenomena in terms of the thermal field, as well as the design and applications of nonreciprocal thermal metamaterials. However, it is crucial to acknowledge that nonreciprocity phenomena extend beyond the thermal field. It also attracts a broader exploration of other physical fields governed by the Laplace equation, such as the electric charge diffusion process. This section is dedicated to elucidating the possibility of nonreciprocity in the thermal field extending to other Laplace physical fields.

For heat, the relevant modulation physical quantities are heat capacity and thermal conductivity. For the diffusion of electric charge, the corresponding physical quantities are capacitance and electrical conductivity. Electric charge diffusion can be macroscopically expressed by Fick's diffusion equation [63]:

$$\frac{\partial q(x,t)}{\partial t} = D\frac{\partial^2 q(x,t)}{\partial x^2} \tag{18}$$

where $D = \sigma g$ is the diffusion coefficient, σ and g are the conductivity and the inverse of the capacity of the medium, respectively, and $q(x,t)$ is charge density. It can be seen that the electric charge diffusion equation (Eq. (18)) has a form similar to that of the heat conduction equation (Eqs. (4) and (6)). Thus, by introducing traveling-wave spatiotemporal modulation to dynamically change the material parameters such as conductivity and capacitance, a nonreciprocal electric charge diffusion process can be realized [63,110]. In Fig. 6(a), a constant voltage source is applied at the left end of the sample, while the right end is kept electrically insulated. The sample consists of 50 disk capacitors that rotate at a constant angular velocity to generate spatiotemporal variation in conductivity and capacitance, which induces an asymmetric transfer of charge.

Besides charge diffusion, Fick's diffusion equation also holds for the mass diffusion process, which is driven by the potential gradient. For instance, metamaterial-based design methods have been designed to realize mass diffusion invisibility cloaks [111–114], concentrators [114], rotators, and material separation devices [115–117]. Fig. 6(b) illustrates a device that integrates a mass diffusion metamaterial with different functions for manipulating ion diffusion in liquids, including a bilayer cloak, a concentrator, and an ion selector [114]. By adjusting the material parameters, it is feasible to realize nonreciprocal material diffusion, allowing the selective transmission of specific substances. Such developments find valuable applications in tasks such as separating mixtures and filtering contaminants, for example, in areas such as wastewater treatment, air filtration, and fractionation.

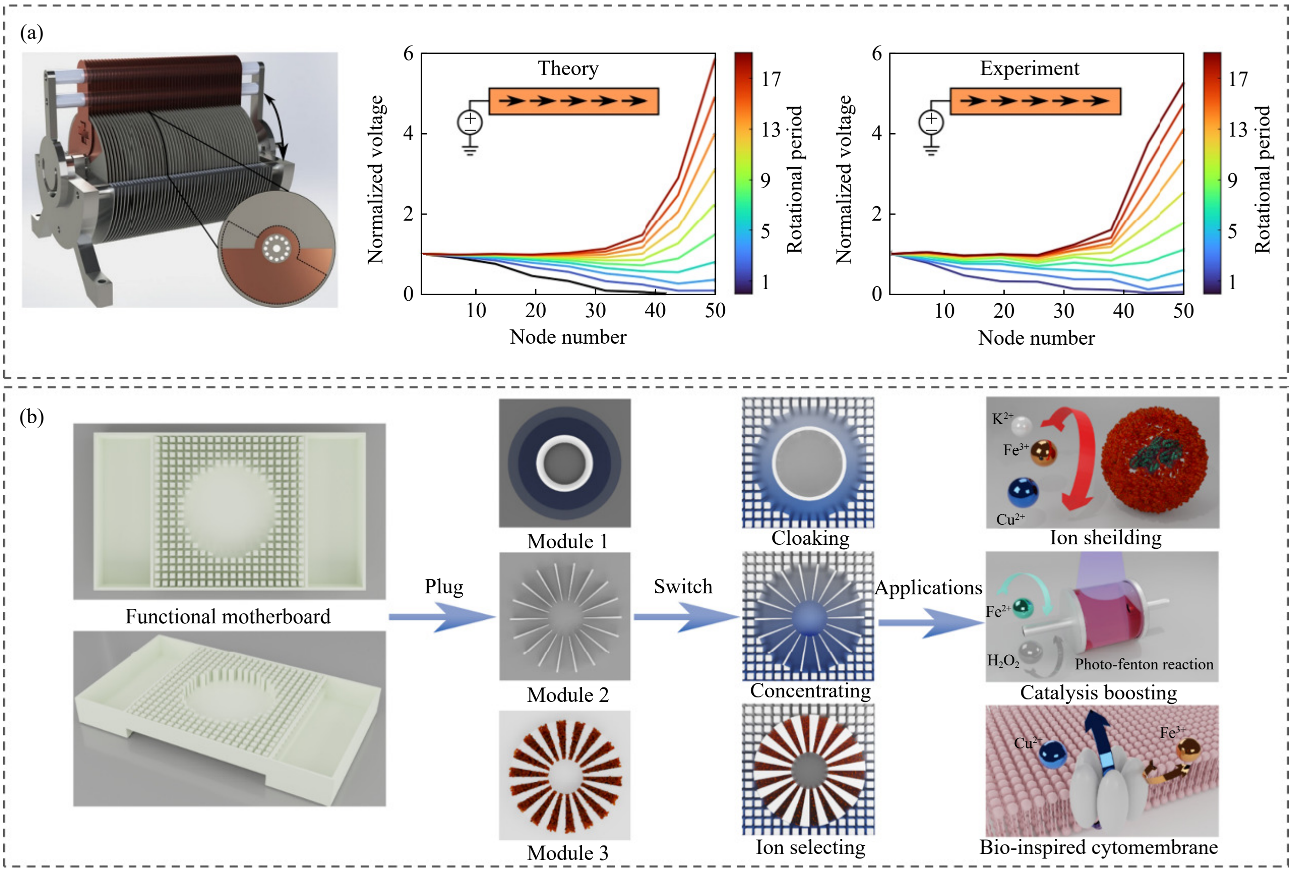

Fig. 6. Metamaterials in the electric charge and mass diffusion process: (a) experimental setup consisting of 50 discs (left), theoretical prediction of the time-average voltage for each disk at each rotational period (middle), and experimental measurement (right) [63]; (b) mass diffusion metamaterials that manipulate the behavior of ion diffusion can realize ion cloaking, concentration, and ion selection in liquid solvents [114].

6. Outlook

This study presents a comprehensive overview of nonreciprocal thermal transfer. First, we present an elaborate explanation of the Onsager reciprocity relation, which is a basic theory in the design of nonreciprocal thermal metamaterials. By considering four key assumptions, we derive the Onsager reciprocal relations and show their application to heat conduction processes. Next, we explore different approaches to breaking reciprocity and extensively discuss three commonly applied methods: nonlinear systems, spatiotemporal modulation, and angular momentum bias.

Nonlinear thermal materials or structures can break the linear response and realize nonreciprocal heat transfer. However, its application is limited by temperature-dependent material parameters. By adjusting the material parameter properties, spatiotemporal modulation induces the breaking of both temporal and spatial inversion symmetry in linear systems. Angular momentum bias leads to a difference in the distribution of angular momentum by introducing rotation, which realizes nonreciprocal heat transfer. These methods give us a higher degree of freedom of thermal field regulation so that thermal metamaterials exhibit several novel applications, such as thermal isolation [73], geometric heat pumps [35], and topological protection [75].

Future research directions are outlined. First, it is imperative to perform extensive studies on the design and preparation methods of nonreciprocal thermal metamaterial devices to address real-life thermal regulation challenges. For example, the development of nonreciprocal thermal radiation devices should progress from the initial single-channel to dual-channel and multichannel systems. To address the demands of more intricate operating environments, dynamically tunable nonreciprocal radiation should also be considered. Integration with other material design approaches should be considered, such as leveraging machine learning for parametric optimization [118]. In addition, synergistic combinations of nonreciprocal thermal metamaterials with advanced materials and technologies such as nanotechnology [119] and photonics [81] hold promise for realizing improved levels of thermal field regulation and application. Finally, it is crucial to examine the potential application of the design methodology applied in nonreciprocal thermal metamaterials to other Laplacian fields, including current and material diffusion fields. To sum up, investigating nonreciprocity in thermal metamaterials provides innovative insights and methodologies for controlling and regulating heat transfer.

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Conflict of Interest

Yang Bai is an editorial board member for this journal and was not involved in the editorial review or the decision to publish this article. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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