Demonstration of room temperature rectification in tapered-channel thermal diodes through confinement-induced liquid-solid phase change

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Designing thermal diodes is attracting a considerable amount of interest in recent times due to the wide range of applications and potentially high impact in the transportation and energy industries. Advances in nanoscale synthesis and characterization are opening new avenues for design using atomic-level physics to take advantage of materials properties in confined volumes. In this paper we demonstrate using advanced modeling and simulation the rectification properties of tapered-channel thermal diodes relying on asymmetric heat flow brought about by thermal conductivity differences between the liquid and solid phases of suitably selected phase-change materials (PCM). Our prototypical design considers Ga as PCM and anodized alumina as structural material. First ,we carry out finite element simulations to study the effect of several geometric parameters on diode efficiency, such as channel length as aspect ratio. We then use a thresholding scheme to solve a Stefan problem in the device channel to study at the hysteresis of the phase transformation when the temperature gradient is switched. Our analysis establishes physical limits on rectification efficiencies and point to design improvements using complex materials to assess the potential of these devices as viable thermal diodes.

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I. INTRODUCTION

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A. Background

While electrical resistors and capacitors have thermal 3 analogs in the form of linear static and passive thermal 4 materials, no such analog exists for diodes and transistors 30 5 (asymmetric heat flow and heat flow on demand). Such 31 6 thermal devices would enable precise control of thermal 32 7 energy transport and would significantly increase the ef- $_{\scriptscriptstyle 33}$ 8 ficiency and compactness of energy conversion and stor- $_{\scriptscriptstyle 34}$ 9 age systems, heating and refrigeration, and thermal man- $_{35}$ 10 agement of electronic devices and spacecrafts. Figure $_{36}$ 11 1 schematically illustrates the transfer function of (a) a $_{37}$ 12 thermal diode and (b) a thermal switch, comparing them $_{38}$ 13 to a passive resistor of thickness L and thermal conduc-14 tivity k [1]. Although the field is attracting significant $_{40}$ 15 research [1-3], discovering new materials with switch-16 able and nonlinear thermal behavior relating to heat flow $_{_{42}}$ 17 (analogous to electric current), or to temperature differ- $_{43}$ 18 ence or thermal bias (analogous to voltage differential) 44 19 still remains elusive due to a number of unresolved chal- $_{\scriptscriptstyle 45}$ 20 lenges. The principal difficulty is how to use standard $_{46}$ 22 thermal transport to achieve nonlinear phenomena such $_{47}$ 23 as thermal *rectification* (i.e., net directional heat flow). $_{_{48}}$ 24 While a number of solutions have been proposed, produc-25 ing rectification coefficients of sufficient magnitude over $_{50}$ 26

a wide temperature window has proven to be difficult [4, 5].

One potential pathway to induce asymmetric heat flow is to take advantage of the thermal conductivity differential between the liquid and solid phases of a given substance [3, 6]. Ideally, materials with fast, reversible, solid-liquid transitions must be used in conjunction with devices that control the phase transition based on the direction of heat flow. As recent research suggests, this can be achieved via nanoscale functional design [7, 8]. The central idea behind these devices is to take advantage of capillary *freezing point depression* of the phasechange material, i.e. achieving the phase transformation at different temperatures depending on whether it initiates from the liquid phase or from the solid phase. This can be achieved by designing a nanoporous material with parallel conical pores that result in a channel radius gradient across the device. The general design is illustrated in Figure 2, where conical channels with variable radius rare infiltrated with a phase-change material (PCM) that coexists in its solid and liquid forms thanks to freezing point depression. The two phases are separated by a curved moving interface that responds to changes in the thermal gradient, $\Delta T = T_h - T_c$. Depending on how this interface evolves, which determines the volume fraction of the liquid (poor thermal diffusivity) vs. the solid (good thermal diffusivity) phases, asymmetric heat flow can be induced.

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FIG. 1. Illustration of the transfer function of (a) ther-⁸² mal diodes and thermal resistors and (b) thermal switch that ⁸³ could be enabled thanks to asymmetric and nonlinear thermal ⁸⁴ behavior of novel materials (adapted from ref. [1]). ⁸⁵

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56 B. Demonstration of concept viability via theory 57 and modeling

Phase change materials undergoing rapid phase switch- 90 58 ing in nano confinement conditions are exceedingly diffi-⁹¹ 59 cult to study experimentally. In this context of extremely 60 fine length and time scales, theory, modeling, and sim-61 ulation are crucial tools to perform a priori analyses of 62 the thermal diode's performance and physical viability. 63 Of special interest is the motion along the channel of 64 the liquid/solid interface in response to the thermal gra- $_{_{92}}$ 65 dient, as its position determines the volume fraction of 66 each phase and -consequently- the efficacy of the thermal 67 conductivity differential. 68 93

This interface moves along either direction of the ta-69 pered channels depending on the sign of the temperature 70 gradient, driven by both the free energy differential be- 94 71 tween the different phases and by curvature. Curvature is 95 72 introduced both via the container design (channel walls) ⁹⁶ 73 and from the liquid-solid interface. This can be modeled 97 74 by solving a Stefan problem using fast and accurate al- 98 75 gorithms for solving singular energy minimization prob- 99 76 lems. The objective of these simulations is to predict the 100 77



FIG. 2. Schematic diagram of the proposed thermal diode design. Conical channels with variable radius r are infiltrated with a phase-change material that coexists in its solid and liquid forms thanks to freezing point depression. The two phases are separated by a curved moving interface that responds to changes in the thermal gradient, $\Delta T = T_h - T_c$, giving rise to asymmetric heat flow.

solidification/melting dynamics of the system, including time response of the phase transition as a function of the material type and thermal gradient amplitude, crystallization microstructure, and possible hysteresis effects due to confinement and nucleation at the channel boundaries. The goal of the modeling effort is to simulate the cyclic response of these devices to variable switching of thermal gradients, as well as to identify suitable material candidates on the basis of their dynamic phase change properties.

Next, we provide a detailed description of the theory behind the models proposed, as well as a quantitative analysis and examples of different candidate materials based on their physical properties.

II. THEORY AND MODELING

A. Stefan Problem with surface tension

The standard formulation of the Stefan problem with surface tension (see for example refs. [9–12]) assumes the existence of a region Ω separated into a solid phase occupying a subregion Ω_s and a liquid phase occupying a subregion Ω_{ℓ} . Ω_s and Ω_{ℓ} are separated by an interface $\Gamma_{s,\ell}$ (cf. Fig. 2). Ω is bounded by an external interface Γ . The evolution of the temperature field in $\Omega \equiv \Omega_s + \Omega_{\ell}$ is 101 governed by:

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$$\frac{\partial T}{\partial t} = \alpha_s \Delta T, \quad \text{in } \Omega_s \tag{1}_{148}^{147}$$

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$$\frac{\partial T}{\partial t} = \alpha_{\ell} \Delta T, \quad \text{in } \Omega_{\ell}$$
(2)

$$T = T_m^* \left(1 - \frac{2\sigma_{s,\ell}}{\Delta h_s} \kappa \right), \quad \text{on } \Gamma_{s,\ell}$$

$$\frac{\partial \Gamma_{s,\ell}}{\partial t} = \Delta h_f^{-1} \left(\alpha_s \frac{\partial T}{\partial n_s} - \alpha_\ell \frac{\partial T}{\partial n_\ell} \right) \tag{4}^{151}$$

where α_s , α_ℓ are the heat diffusivity constants of the solid¹⁵⁴ 106 and liquid phase, Δh_f is the specific latent heat of fusion,¹⁵⁵ 107 T_m^* is the melting temperature, n is the unit normal to¹⁵⁶ 108 Γ pointing away from Ω_s and n_s and n_ℓ denote that the $^{\rm 157}$ 109 limit is taken either on the solid or liquid side. $\kappa = \kappa(x)^{158}$ 110 is the mean curvature of $\Gamma_{s,\ell}$ at a point $x \in \Gamma_{s,\ell}$ with¹⁵⁹ 111 the convention that $\kappa \geq 0$ if the solid region is convex.¹⁶⁰ 112 The temperature condition on the interface is the classic¹⁶¹ 113 Gibbs-Thompson law [13, 14], with $\sigma_{s,\ell} > 0$ the surface¹⁶² 114 tension of the solid/liquid interface. 163 115

The above model can be augmented by assuming that the solid and liquid phases have surface energy interactions with the container wall. It can be then shown [15] that the surface tension must satisfy the triangle inequalities

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$$\sigma_{\ell,w} \le \sigma_{s,w} + \sigma_{s,\ell}.\tag{6}$$

 $\sigma_{s,w} \le \sigma_{\ell,w} + \sigma_{s,\ell}$

where $\sigma_{s,w}, \sigma_{\ell,w}$ are the surface tension at the interfaces 124 between the wall and the solid and liquid, respectively, 125 and $\Gamma_{s,w}, \Gamma_{\ell,w}$ are the interfaces between the wall and 126 the solid and liquids respectively. Failure to satisfy these 127 inequalities gives rise to the possibility of nucleation of 128 one phase within the other. By way of example, if in-164 129 equality (5) is not satisfied, it is energetically favorable₁₆₅ 130 for an arbitrarily thin region of liquid phase to nucleate¹⁶⁶ 131 between any contact surface of the solid and the wall. 167 132 In addition, at the point where the two phases and 168 133 the wall meet, the system of equations (1)-(4) must be₁₆₉ 134 complemented with the so called *Herring* angle condition¹⁷⁰ 135 136 [16]: 171

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$$\theta = \frac{\pi}{2} \left(1 + \frac{\sigma_{s,w} - \sigma_{\ell,w}}{\sigma_{s,\ell}} \right)$$
(7)¹⁷³
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(7)¹⁷³
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where θ is the opening angle of the intersection of the¹⁷⁵ solid-wall and solid-liquid interfaces measured from in-¹⁷⁶ side the solid phase. Note that the triangle inequalities¹⁷⁷ for the different surface tensions ensure that the angle is¹⁷⁹ always between 0 and π .

143 B. Particularities of conically tapered channels

The system of eqs. (4) to (7) is now solved in a tapered conical channel of the type shown schematically¹⁸⁵

in Fig. 2. Assuming that the interface equilibrates to constant curvature, one can derive from eqs. (3) and (7) an expression for the so-called *freezing point depression*, i.e., a size dependent T_m^* :

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150 (3)

(5)

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$$T_m^*(r) = T_m^0 \left(1 - \frac{2\sigma_{s/\ell,w}}{r\Delta h_f} \right) \quad \text{on } \Gamma \tag{8}$$

where T_m^0 is the bulk melting temperature, $\sigma_{s/\ell,w}$ is a coefficient that accounts for the relative affinity of the solid 's' and liquid ' ℓ ' phases for the container wall, and where it has been assumed that $\kappa \propto r^{-1}$ is the curvature of any annular section of constant radius r of the cone. As explained in Sec. I A, the efficacy of our thermal diode design is predicated on the ratio k_ℓ/k_s . Note that, for clarity, in this section we work with the thermal conductivities $k_{\ell,s} = \alpha \rho C_p|_{\ell,s}$, where ρ and C_p are the mass density and the heat capacity of the corresponding liquid or solid phase. Table I lists a number of candidate PCMs with their corresponding bulk melting temperatures and ordered by increasing thermal conductivity ratio. As the

TABLE I. List of candidate PCMs with their corresponding bulk melting temperatures, ordered by their thermal conductivity ratio. Temperatures are in degrees Celsius and thermal conductivities in $W \cdot m^{-1} \cdot K^{-1}$ (from various sources, [17]).

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PCM	T_m^0	k_s	k_ℓ	k_ℓ/k_s
Al	657	218	94	0.43
Cu	1090	339	166	0.49
Sn	220	60	30	0.49
Ga	30	42	25	0.59
$\mathrm{Bi}_{50}\mathrm{Pb}_{27}\mathrm{Sn}_{13}\mathrm{Cd}_{10}$	70	33	22	0.68
CdZn	266	86	60	0.70
$\mathrm{Sn}_{60}\mathrm{Bi}_{40}$	200	27	19	0.70
SnCu	227	59	45	0.76
ZnMg	366	137	107	0.78
SnPb	183	40	32	0.80

data in the table reveal, some PCMs display significant thermal conductivity decreases upon melting. More importantly, the thermal conductivity differential is highest for the pure metals Al, Cu, Sn, and Ga. However, substances whose solid/liquid transition occurs near room temperature are of particular interest in this work, as they offer a potentially wider range of applicability. Of those shown in the table, Ga is the option with the best combination of melting temperature and low k_{ℓ}/k_s ratio. Figure 3 shows measurements of k_s and k_{ℓ} for commercial Ga [18, 19], showing the gap between the solid and liquid phases. The behavior for the other pure metals is found to be qualitatively very similar.

Taking advantage of the k_{ℓ}/k_s ratio is also important for our design to find materials with the highest melting point differential $\Delta T^{\rm fr} = T_m^*(r) - T_m^0$. One can obtain estimates for $\Delta T^{\rm fr}$ directly from eq. (8) using the parameters of Table II:

$$\Delta T^{\rm fr} = \frac{2T_m^0 \sigma_{s,\ell} \cos \theta}{r \rho_s \Delta h_f} \tag{9}$$



FIG. 3. Evolution of the thermal conductivity of pure Ga as a function of temperature. The dashed line marks the melting point, at which a noticeable drop is observed [18, 19].

where ρ_s is the density of the solid phase. For the moment, we assume that $\sigma_{w,s/\ell} = \sigma_{s,\ell} \cos \theta$ (recall that θ here is the angle from the Herring angle condition (7)).

Published values for the rest of the parameters in eq. (9) are given in Table II. From those, we get the dependence of the freezing point depression with section radius shown in Figure 4 as given by: 194

TABLE II. Values for the parameters used in eqs.(4) and (9)¹⁹⁶ for Ga (from refs. [20–22]). Note that, for the different surface¹⁹⁷ tensions given, the Herring angle is 27.5° according to eq. (7).¹⁹⁸

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constant	units	value	
T_m^0	Κ	302.8	
$\sigma_{s,\ell}$	$\mathrm{J}~\mathrm{m}^{-2}$	0.056	
$\sigma_{s,w}$	$\mathrm{J}~\mathrm{m}^{-2}$	1.63	
$\sigma_{\ell,w}$	$\mathrm{J}~\mathrm{m}^{-2}$	1.80	
θ	deg	30	
ρ	${ m g~m^{-3}}$	5.91×10^6	
Δh_f	$\rm J~g^{-1}$	80.4	

$$\Delta T^{\rm fr} = 6.16 \times 10^{-8} r^{-1}$$

with ΔT^{fr} in K when r is in m. The graph suggests that channels with cross sections smaller than 5-nm in radius are needed to take advantage of freezing point depression (12.5 K at r = 5 nm).

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Our numerical approach to solving eqs. (4) is based on an iterative energy minimization scheme of a nonlocal surface energy functional \mathcal{H}_{ϵ} . To that end, let now Ω_s ,



FIG. 4. Freezing point depression in Ga as a function of the radius of curvature.

 Ω_{ℓ} , and Ω_{w} specifically denote the volume fractions of the solid, liquid, and outer wall regions (see Fig. 2):

$$\mathcal{H}_{\epsilon}(\Omega_{s}, \Omega_{\ell}, \Omega_{w}) = \frac{1}{\sqrt{\epsilon}} \left[\sigma_{s,\ell} \int_{\Omega} \Omega_{\ell}(x) (H_{\epsilon} * \Omega_{s})(x) \, dx + \int_{\Omega} (\sigma_{s,w} \Omega_{s}(x) + \sigma_{\ell,w} \Omega_{\ell}(x)) (H_{\epsilon} * \Omega_{w})(x) \, dx \right]$$
(10)

where H_{ϵ} is a heat kernel [23] that is convolved in space with each of the Ω_{α} at time $t = \epsilon$. Integration in the above equations is understood to occur over the entire configurational volume (dx is shorthand notation for an infinitesimal volume element). When ϵ tends to zero, the heat content energy converges to the usual surface tension energy [24]. Note that the outer pore walls are fixed, hence Ω_w cannot change over time. Furthermore, in the pore interior, we must have the relation $\Omega_s + \Omega_{\ell} = 1$. Thus, we only need to keep track of the relative concentration of the solid phase. Thus we write $\Omega = \Omega_s$ and view the functional $\mathcal{H}_{\varepsilon}$ as a function of Ω only.

The solver employed to minimize the above functional is based on a *thresholding* scheme, the likes of which have proven to be robust methods for dealing with sharp interfaces [24–26]. At a step *i* with known temperature and concentration of the solid phase (T^i and Ω^i , respectively), we obtain T^{i+1} and Ω^{i+1} via the following three steps:

$$T^{i+\frac{1}{2}} - T^{i} = \tau \nabla \cdot \left(\left[\alpha_{s} \Omega^{i} + \alpha_{\ell} (1 - \Omega^{i}) \right] \nabla T^{i+\frac{1}{2}} \right) (11)$$
$$\Omega^{i+1} = \text{Thresh} \left(\Omega^{i} + \frac{T_{m} \exp\left(-\frac{1}{\Delta h_{f}} \mathcal{H}_{\epsilon}(\Omega^{n}) \right) - T^{i+\frac{1}{2}}}{\Delta h_{f}} \right) (12)$$
$$T^{i+1} = T^{i+\frac{1}{2}} + \Delta h_{f} (\Omega^{i+1} - \Omega^{i})$$
(13)

As in Sec. II A, α_s and α_ℓ are the heat diffusivities of the solid and liquid phases, Δh_f is the latent heat of fusion,

 τ is the time step, and for any real-valued number *a*:

Thresh(a) =
$$\begin{cases} 0 & \text{if } a < 0, \\ a & \text{if } a \in [0, 1], \\ 1 & \text{if } a > 1. \end{cases}$$

Equation (11) is an approximation to the evolution of 216 the heat equation for time τ . Note that equation (11) 217 takes into account the difference in thermal conductivity 218 between the solid and liquid phases. The expression for 219 the second step, eq. (12), comes from the solution of a 220 variational problem that ensures that the scheme above 221 is unconditionally stable. Roughly, eq. (12) balances the 222 competing effects of surface tension and melting tempera-223 ture on the relative concentrations of the solid and liquid 224 phases. The final step, eq. (13), updates the temper-225 ature by taking into account the heat that is released 226 (absorbed) by freezing (melting). 227

One of the advantages of this approach is that the Gibbs-Thompson condition [given in eq. 4] at the interface is encoded in the update steps (12) and (13), without needing to be explicitly defined.

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III. RESULTS

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Next we present results for the Ga-Al₂O₃ tapered chan- 262 nel design described above.

235 A. Rectification and optimum thermal diode design

The initial geometry of the thermal diode building 236 block structure can be optimized to maximize the rec-237 tification, i.e., the ratio of heat fluxes in the forward and 238 reverse directions for given thermal conductivities of the 239 substrate solid and liquid phases, and melting tempera-240 ture of the PCM filling the conical channel. This rectifi-241 cation can be obtained by solving the system of equations 242 (1)-(4) in geometries such as that provided in Fig. 2 sub-243 jected to a prescribed temperature gradient. The goal in 244 this section is to optimize the aspect ratio of the tapered 245 channels [28] for a fixed channel length to maximize rec-246 tification and guide synthesis processes. 247

To that end, we use the finite element code Abaqus 248 in geometries defined by a total channel length L = 400249 nm, and a radius at the narrow end of the conical section 250 of $r_2 = 5$ nm. The wide-end radius is left as an out-251 come of the maximization exercise, but we set its mini-252 mum value to $r_1 = 40$ nm. The temperature window is 253 always centered at T_m^0 , and we use a thermal conductiv-254 ity for an odized alumina of 1.0 $\mathrm{W}{\cdot}\mathrm{m}^{-1}{\cdot}\mathrm{K}^{-1}$ [29]. Figure 255 5 shows the rectification behavior for the $Ga-Al_2O_3$ ta-256 pered channel design with $r_2/r_1 = 40/5$, with the shaded 257 areas in each quadrant of the graph giving the range of²⁶⁶ 258 attainable rectifications. The dotted lines mark the ideal₂₆₇ 259 rectification as set by a full solid phase (forward ther-268 260 mal gradient) or a full liquid phase (reverse gradient) of₂₆₉ 261



FIG. 5. Abaqus (finite element) calculations of the rectification effect for the Ga-Al₂O₃ tapered channel design with $r_2/r_1 = 40/5$ proposed in this work. The shaded areas in each quadrant of the graph give the range of attainable rectifications. The dotted lines mark ideal rectification as set by a full solid phase (forward thermal gradient) or a full liquid phase (reverse gradient). The heat flux is multiplied times the length of the tapered channel (400 nm) and thus given in W·m.

the PCM in the channel. Figure 6 shows color maps of the steady-state temperature and heat flux fields for the same design as in Fig. 5 when in the reverse configuration (heat flowing towards the left).



FIG. 6. Color maps in arbitrary units of the steady state Abaqus solutions for the 40/5 diode (L = 400 nm). (a) Temperature field. (b) Heat flux. Both images are for forward conduction.

The data in Fig. 5 were used to calculate the rectification R of the device, obtained using a widely-accepted 270 definition for R [1, 30, 31]:

$$R = \frac{\dot{Q}_f}{\dot{Q}_r} - 1 \tag{14}$$

The results are shown in Figure 7, where a gradual in-272 crease in R is seen up to $\Delta T = 22$ K when the maximum 273 value of 21 % is reached. While these are the actual 274 values for the specific design proposed here, note that 275 the maximum (theoretical) rectifications attainable are 276 those corresponding to heat fluxes on the boundaries of 277 the shaded regions in Fig. 5 (marked by dotted lines), cor-278 responding to R = 68 %. Consequently, one can propose 279



FIG. 7. Device rectification calculated with eq. (14) using the data in Fig. 5.

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²⁸² a rectification *efficiency*, based on the relative 'distance' ²⁸³ of the simulated curve to the ideal limits [3]:

$$\eta = \sum_{i}^{N} \left(1 - \frac{\left| \dot{Q}_{s}^{\text{sim}} - \dot{Q}_{s,\ell}^{\text{id}} \right|}{\left| \dot{Q}_{s}^{\text{id}} - \dot{Q}_{\ell}^{\text{id}} \right|} \right) \tag{15}_{300}$$

where N is the total number of data points, and $\dot{Q}^{\rm id}$ and 308 285 $\dot{Q}^{\rm sim}$ are the ideal and simulated heat fluxes for a given³⁰⁹ 286 ΔT . With this definition, points lying on the dotted lines³¹⁰ 287 in Fig. 5 would give an efficiency of 100%. The efficien-288 cies are averaged across all ΔT -points for each branch, 289 so that we have distinct forward and reverse efficiencies.³¹¹ 290 For the design considered here, $\eta \approx 99\%$ for the reverse³¹² 291 configuration (all liquid) and $\approx 21\%$ for the forward di-292 rection (partially liquid and solid). 313 293

Next, we carry out several simulations varying r_1 and r_1 L to calculate the associated efficiencies as optimization several simulation in Table III. The rectification efficiency is practi- r_1 cally independent of the total length L of the thermal diode. Similarly, η_f appears to be quite insensitive to r_1 the value of r_1 above approximately 40 nm. Figure 8220

TABLE III. Rectification efficiency as determined using eq. (15) for the 'forward' and 'reverse' branches of the thermal diode design as a function of the large end radius r_1 and total length L of the conical channel. r_2 is fixed at 5 nm here.

L =	= 400	nm	
$r_1 [\mathrm{nm}]$	20	40	60
$\eta_{\rm f}$ [%]	15	21	26
$\eta_{\rm r}$ [%]	100	99	98
$r_1 = 40 \text{ nm}$			
L [nm]	100	200	400
$\eta_{\rm f}$ [%]	22	21	21
$\eta_{ m r}$ [%]	99	99	99

shows the evolution of the $\eta_{\rm f}$ - r_1 relationship for r_1 in the 20-to-400-nm interval.



FIG. 8. Rectification efficiency along the conducting ('forward') direction of the thermal diode design proposed in this work as a function of the large conical radius r_1 . All data points are for fixed values of $r_2 = 5$ nm and L = 400 nm.

These findings point towards designs with aspect ratios r_1/r_2 larger than 40/5. However, as long as that condition is satisfied, the large radius of the tapered conical channel can be flexibly selected on the basis of device synthesis considerations.

B. Modeling solid/liquid interface effects and thermal gradient hysteresis

While the above results are useful to gain insight into the global behavior of the thermal diode design, they ignore critical physical processes that take place at the solid/liquid interface. For example, the finite element calculations assume a flat solid/liquid interface that responds symmetrically to switching the thermal gradient. However, it is known that contact effects and surface tension break the directional symmetry of the interface with respect to the direction of heat flow. In this section we study the physical behavior of the s/ℓ interface solving the Stefan problem defined in eqs. (4) explicitly by following the numerical procedure described in Section II C. We restrict our study to the thermal diode design with $L = 400 \text{ nm and } r_1/r_2 = 40/5.$



FIG. 9. Stationary state of a Stefan problem with fixed temperature values on the boundary. The white, blue and brown regions represent the solid, liquid and pore walls respectively. (a) The temperature on the left-hand side boundary of the pore is lower than the temperature on the right-hand side boundary (260 vs. 340 K). The device is the 'forward' position, allowing heat to quickly flow from the right-hand side to the left. (b) The device is in the 'reverse' position, and heat is transferred more slowly from the left-hand side to the right compared to the situation in (a).

327 We begin by studying the steady state of a Stefan prob-

lem with fixed temperature values on the boundary. In³⁵⁷ 328 the following figures, the white, blue and brown regions³⁵⁸ 329 represent, respectively, the solid (Ω_s) , liquid (Ω_{ℓ}) , and³⁵⁹ 330 pore walls (Ω_w) . Figure 9 gives the converged solution³⁶⁰ 331 for the 'forward' (heat flowing from right to left) and 're-³⁶¹ 332 verse' (left to right) cases. For Fig. 9(a), the temperature³⁶² 333 on the left boundary of the pore is lower than the temper-³⁶³ 334 ature on the right (260 vs. 340 K). The temperatures on³⁶⁴ 335 each side are sufficiently low to prevent complete melt-³⁶⁵ 336 ing of the solid phase. As a result the device is in the³⁶⁶ 337 'forward' position, allowing heat to quickly flow from the³⁶⁷ 338 right to left. In Fig. 9(b), the temperature boundary con-³⁶⁸ 339 dition is reversed with respect to 9(a). Due to the melting³⁶⁹ 340 point depression effect, the solid completely melts in the³⁷⁰ 341 narrow part of the pore on the left-hand side and, as a³⁷¹ 342 result, the device is in the 'reverse' position with heat be-372 343 ing transferred from left to right more slowly than in the³⁷³ 344 inverse situation. In both cases, notice how the relative³⁷⁴ 345 balance of surface energies makes the interface curvature³⁷⁵ 346 always concave with respect to the origin at the center 347 of the narrow end of the channel. 348

Perhaps more interesting is to study the dynamic₃₇₇ 349 asymmetry between the melting and solidification pro-378 350 cesses when the temperature gradient is reversed. This is₃₇₉ 351 illustrated graphically in Figure 10, where the interface₃₈₀ 352 position is tracked as it evolves in response to thermal₃₈₁ 353 switching. In Fig. 10(a), solidification of the liquid phase₃₈₂ 354 is shown when the temperature at the right boundary is₃₈₃ 355 fixed at 20 K below T_m^0 . The white region in the cen-₃₈₄ 356



FIG. 10. (a) Solidification of the liquid phase when the temperature at the right-hand side boundary is fixed at 20 K below the melting point. The white region in the center is the part of the pore that is initially in the solid phase. The next lightest region solidifies in the first 5 seconds of the evolution, and so on. Steady state is reached after 15 seconds, when the solid fills all of the pore except for the darkest blue region. (b) Melting of the solid phase when the temperature at the right-hand side boundary is fixed at the melting point. Initially, the entire pore is solid. The darkest blue region melts in the first 5 seconds of the evolution. The next darkest region melts during in the next 5 s, etc. The white region in the center remains solid after 25 seconds have elapsed.

ter is the part of the pore that is initially in the solid phase. The next lightest region solidifies in the first 5 seconds of the evolution and so on. The steady state is reached when the solid fills all of the pore except for the darkest blue region, after approximately 15 s. In Fig. 10(b), the temperature gradient is inverted and the melting front is tracked and plotted in five-second intervals. The white region in the center remains solid after 25 s, when steady state is reached. This clearly points to an asymmetry along the direction of propagation of the front, which can be appreciated in Figure 11. The figure shows a quasi-hysteresis cycle encompassing 25 seconds of forward thermal switching (inducing solidification) followed by an equal amount of time under the reverse gradient. As seen in the figure, at the end of the melting stage the front is found at some distance away from the base of the conical channel. The slopes of the blue and red branches give the velocities of propagation of the interface at each time.

Ideally, these results can be used to inform the finiteelement calculations shown in Fig. 6 so as to create a self-consistent feedback loop that yields converged rectification factors when the shape and dynamics of the interface are taken into account. We consider such exercise to be beyond the present scope of this study (although we speculate that it may lead to slightly lower rectifications due to the convex shape of the interface).



FIG. 11. Position of the center point (on long axis of the $^{\rm 433}$ conical channel) in units of L of the solid/liquid interface as $^{\rm 434}$ a function of time for a full thermal switching cycle. Time⁴³⁵ 436 follows the direction of the arrows.

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IV. DISCUSSION

Numerical demonstration of rectification and Α. 386 hysteresis 387

This work is essentially a numerical demonstration of⁴⁴¹ 388 net rectification in conical tapered channels containing a⁴⁴² 389 phase-change material enclosed in a nanoscale architec-443 390 ture made up of a thermal insulating material. On the444 391 basis of this design, we can act on different degrees of⁴⁴⁵ 392 freedom to increase rectification: 393

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394	1. On the materials side, the use of PCMs with the $_{448}$
395	widest difference between the liquid and solid ther-
396	mal conductivities yields the widest possible recti-449
397	fication range (see shaded regions in Fig. 5).
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- 2. On the geometry side, the ideal design is that whose 398 forward and reverse thermal biases can come closest⁴⁵¹ 399 to the pure liquid and solid limits. For this, the⁴⁵² 400 geometry that best takes advantage of the freezing 401 point depression emanating from nano-confinement $^{\scriptscriptstyle 453}$ 402 of the PCM in tapered channels is one with a high $^{\rm 454}$ 403 455
- r_1 -to- r_2 ratio. 404 456

While these considerations pertain to static properties⁴⁵⁷ 405 of the device, dynamic effects must also be considered⁴⁵⁸ 406 as part of the design/operation process. In particular,459 407 the nature of the s/ℓ interface and its propagation in⁴⁶⁰ 408 the forward and reverse directions is seen to control the 409 speed of the transformation and the capability to fully 410 achieve the theoretical efficiency as presented in, e.g.,⁴⁶¹ 411 Fig. 8. As demonstrated in Sec. III B, the surface tension 412 between the solid, liquid, and channel wall materials con-462 413 trols the s/ℓ interface curvature, which in turn results in 414 a propagation asymmetry between the forward and re-463 415 verse thermal gradient directions. This asymmetry gives₄₆₄ 416 rise to a hysteresis cycle that must be carefully studied to₄₆₅ 417 avoid long-term detrimental effects associated with ther-466 418

mal and mechanical fatigue, which could eventually lead 419 to device failure.

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While the present design based on porous alumina infiltrated with metallic gallium is suitable for operation near room temperature, other concepts based on 3D nanoscale architectures for higher temperatures can also be considered. As Table I suggests, materials such as Al and Cu have the potential for higher rectification efficiencies when operated at higher temperatures, such that thermal diode designs where these materials act as the PCM may show promise for tapered conical geometries. Eutectic phases of the materials listed in Table I with melting temperature above 500°C and relatively high thermal conductivities (e.g., $>20\sim40 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) may also be considered as alternate phase-change materials. Hightemperature thermal diodes, however, may be susceptible to oxidation, which adds another dimension to the design space.

В. Potential pathways for material selection and synthesis

The initial synthesis and model materials envisioned could consist of synthesizing tapered pores by nonconformal deposition of an insulating material (such as alumina) using a combined atomic layer and chemical vapor deposition (ALD/CVD) method in anodic alumina membranes with cylindrical pores. Then, the tapered pores are infiltrated with eutectic liquid metal alloys such as those of gallium (Ga), indium (In), and tin (Sn). The degrees of freedom in the thermal diode synthesis would include:

- (i) Porosity control via anodic etching conditions.
- (ii) Control of porosity gradient via ALD/CVD.
- (iii) Control of melting temperature (via eutectic composition and PCM nano confinement).

In addition, ALD/CVD can provide control of the thermal resistance between the low thermal conductivity alumina and the high thermal conductivity PCM.

Finally, other geometry concepts may be explored. For example, templated nanoporous silicon carbide (SiC) with spherical pores infiltrated with molten salts may constitute attractive alternatives to the conical channel designs explored in this paper.

v. CONCLUSIONS

Our main conclusions are listed below:

1. We have demonstrated the room temperature rectification of gallium-infiltrated Al₂O₃ taperedchannel thermal diodes through confinementinduced liquid-solid phase change.

- 2. The design relies on the onset of asymmetric heat482
 flow due to a thermal conductivity differential (Fig.483
 3) between the solid and liquid phases of a suit-484
 able phase-change material that undergoes a phase485
 transformation in the temperature range of opera-486
 tion of the thermal diode (Fig. 4).
- 3. Finite-element calculations indicate that, for the prototypical design with L = 400 nm, $r_1 = 40$ nm, and $r_2 = 5$ nm, a maximum rectification of 21 % is achieved (Fig. 7). The maximum theoretical rectification for this design is 68 %.
- 478 4. Above 25 nm, the value of r_1 has practically no ef-479 fect on the thermal efficiency of the thermal diode.
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 5. Modeling of the solid/liquid interface and its in-492
 481 teractions with the channel walls suggests convex493

shapes and a hysteretic dynamic cycle with equilibration times of 25 s (Figs. 9, 10, and 11). The models involve fast interface tracking algorithms using thresholding techniques to solve Stefan problems.

6. Our results can be used as a springboard to consider other PCM that can operate at elevated temperatures with higher rectifications.

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- 494 [1] G. Wehmeyer, T. Yabuki, C. Monachon, J. Wu, and 534
 495 C. Dames, Thermal diodes, regulators, and switches: 535
 496 Physical mechanisms and potential applications, Applied 536
 497 Physics Reviews 4, 041304 (2017). 537
- [2] B. Li, L. Wang, and G. Casati, Thermal diode: Recti-538
 fication of heat flux, Physical review letters 93, 184301539
 (2004). 540
- [3] P. Ben-Abdallah and S.-A. Biehs, Phase-change radia-541
 tive thermal diode, Applied Physics Letters 103, 191907542
 (2013). 543
- [4] E. Pereira and R. R. Ávila, Increasing thermal rectifica-544
 tion: Effects of long-range interactions, Physical Review545
 E 88, 032139 (2013).
- T. Hess, L. Maier, P. Corhan, O. Schäfer-Welsen,⁵⁴⁷
 J. Wöllenstein, and K. Bartholomé, Modelling cascaded⁵⁴⁸
 caloric refrigeration systems that are based on thermal⁵⁴⁹
 diodes or switches, International Journal of Refrigeration⁵⁵⁰
 103, 215 (2019).
- [6] A. L. Cottrill and M. S. Strano, Analysis of thermal⁵⁵²
 diodes enabled by junctions of phase change materials,⁵⁵³
 Advanced Energy Materials 5, 1500921 (2015).
- [7] C. B. Sobhan and G. P. Peterson, Microscale and⁵⁵⁵
 nanoscale heat transfer: fundamentals and engineering⁵⁵⁶
 applications (CRC Press, 2008).
- [8] T. Luo and G. Chen, Nanoscale heat transfer-from com-558
 putation to experiment (2013).
- [9] L. Caffarelli and L. Evans, Continuity of the temperature⁵⁶⁰
 in the two-phase stefan problem, Archive for Rational⁵⁶¹
 Mechanics and Analysis 81, 199 (1983).
- [10] I. I. Danilyuk, On the stefan problem, Russian Mathe-563
 matical Surveys 40, 157 (1985).
- [11] A. Visintin, Stefan problem with surface tension,⁵⁶⁵
 in Mathematical Models for Phase Change Problems⁵⁶⁶
 (Springer, 1989) pp. 191–213.
- [12] A. M. Meirmanov, *The Stefan Problem*, Vol. 3 (Walter⁵⁶⁸
 de Gruyter, 2011).
- [13] Z. Liu, K. Muldrew, R. G. Wan, and J. A. W. Elliott, 570
 Measurement of freezing point depression of water in 571
 glass capillaries and the associated ice front shape, Phys. 572
 Rev. E 67, 061602 (2003). 573

- [14] F. Liu, L. Zargarzadeh, H.-J. Chung, and J. A. Elliott, Thermodynamic investigation of the effect of interface curvature on the solid–liquid equilibrium and eutectic point of binary mixtures, The Journal of Physical Chemistry B 121, 9452 (2017).
- [15] B. Widom, Interfacial tensions of three fluid phases in equilibrium, The Journal of Chemical Physics 62, 1332 (1975).
- [16] C. Herring, Some theorems on the free energies of crystal surfaces, Physical review 82, 87 (1951).
- [17] M. R. Landry, Thermoporometry by differential scanning calorimetry: experimental considerations and applications, Thermochimica acta 433, 27 (2005).
- [18] M. Duggin, The thermal conductivity of liquid gallium, Physics Letters A 29, 470 (1969).
- [19] R. Powell, M. J. Woodman, and R. Tye, Further measurements relating to the anisotropic thermal conductivity of gallium, British Journal of Applied Physics 14, 432 (1963).
- [20] D. Turnbull, Formation of crystal nuclei in liquid metals, Journal of Applied Physics 21, 1022 (1950).
- [21] D. P. Woodruff and D. P. Woodruff, The solid-liquid interface (CUP Archive, 1973).
- [22] M. Losurdo, A. Suvorova, S. Rubanov, K. Hingerl, and A. S. Brown, Thermally stable coexistence of liquid and solid phases in gallium nanoparticles, Nature materials 15, 995 (2016).
- [23] Typically a Gaussian of the form: $H_{\epsilon} = (\epsilon)^{-2} \exp(-\pi |x|^2/\epsilon^2).$
- [24] S. Esedolu and F. Otto, Threshold dynamics for networks with arbitrary surface tensions, Communications on Pure and Applied Mathematics 68, 808 (2015), https://onlinelibrary.wiley.com/doi/pdf/10.1002/cpa.21527.
- [25] Gallouët, Thomas, Laborde, Maxime, and Monsaingeon, Léonard, An unbalanced optimal transport splitting scheme for general advection-reaction-diffusion problems, ESAIM: COCV 25, 8 (2019).
- [26] M. Jacobs and F. Léger, A fast approach to optimal transport: The back-and-forth method, arXiv preprint arXiv:1905.12154 (2019).

tructure, Applied Physics Letters 109, 123106 (2016).

- F. Otto, The geometry of dissipative evolution equations:586
 the porous medium equation, Comm. Partial Differential587
 Equations 26, 101 (2001).
- ⁵⁷⁷ [28] Defined here as the ratio of the radius of the wide sec-⁵⁷⁸ tion of the conical channel r_1 to the radius of the narrow ⁵⁷⁹ section r_2 , r_1/r_2 .
- [29] J. Lee, Y. Kim, U. Jung, and W.-S. Chung, Thermal conductivity of anodized aluminum oxide layer: The effect of electrolyte and temperature, Materials Chemistry and Physics 141, 380 (2014).
- [30] A. Ghanekar, J. Ji, and Y. Zheng, High-rectification near field thermal diode using phase change periodic nanos-
- [31] B. Li, L. Wang, and G. Casati, Thermal diode: Rectification of heat flux, Phys. Rev. Lett. 93, 184301 (2004).