

Thermal Conductivity in Nanostructured Films: From Single Cellulose Nanocrystals to Bulk Films

Jairo A. Diaz,[†] Zhijiang Ye,[‡] Xiawa Wu,[§] Arden L. Moore,^{||} Robert J. Moon,^{*,†,⊥} Ashlie Martini,^{*,‡} Dylan J. Boday,^{*,||} and Jeffrey P. Youngblood^{*,†}

[†]School of Materials Engineering, Purdue University, 701 West Stadium Avenue, West Lafayette, Indiana 47907, United States

[‡]School of Mechanical Engineering, University of California, Merced, California 95343, United States

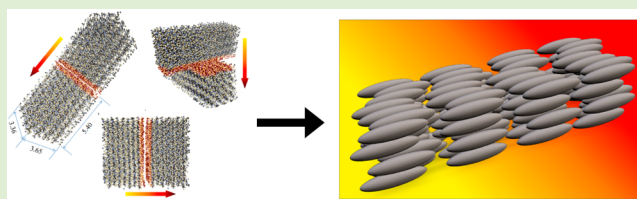
[§]School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, United States

^{||}IBM Materials Engineering, Tucson, Arizona 85744, United States

[⊥]Forest Products Laboratory, U.S. Forest Service, One Gifford Pinchot Drive, Madison, Wisconsin 53726, United States

Supporting Information

ABSTRACT: We achieved a multiscale description of the thermal conductivity of cellulose nanocrystals (CNCs) from single CNCs ($\sim 0.72\text{--}5.7\text{ W m}^{-1}\text{ K}^{-1}$) to their organized nanostructured films ($\sim 0.22\text{--}0.53\text{ W m}^{-1}\text{ K}^{-1}$) using experimental evidence and molecular dynamics (MD) simulation. The ratio of the approximate phonon mean free path ($\sim 1.7\text{--}5.3\text{ nm}$) to the lateral dimension of a single CNC ($\sim 5\text{--}20\text{ nm}$) suggested a contribution of crystal–crystal interfaces to polydisperse CNC film’s heat transport. Based on this, we modeled the thermal conductivity of CNC films using MD-predicted single crystal and interface properties along with the degree of CNC alignment in the bulk films using Hermans order parameter. Film thermal conductivities were strongly correlated to the degree of CNC alignment and the direction of heat flow relative to the CNC chain axis. The low interfacial barrier to heat transport found for CNCs ($\sim 9.4\text{ to }12.6\text{ m}^2\text{ K GW}^{-1}$), and their versatile alignment capabilities offer unique opportunities in thermal conductivity control.



INTRODUCTION

The increasing interest in flexible electronics has pushed development of new nanomaterials that provide seamless integrated structure–property interactions required for a variety of new, efficient configurations in electronic devices (e.g., organic solar cells, organic light emitting diodes, etc.). Of particular interest is the development of materials with high flexibility, impact strength, and transparency with tailored stiffness, thermal expansion, and thermal conductivity to minimize stability problems at interfaces within the electronic architectures. While a broad number of materials are being investigated in this regard, cellulose derivatives^{1–4} represent attractive candidates due to their abundant, renewable, and sustainable character.⁵ Particularly, the unique set of properties exhibited by cellulose nanocrystals (CNCs), rod-like nanoparticles ($\sim 5\text{--}20\text{ nm}$ wide, $\sim 50\text{--}500\text{ nm}$ long),⁶ greatly expand the range of attainable properties and potential applications⁷ due to their intrinsic high anisotropy (Figure 1a) and remarkable organization capabilities.^{6,8} In the presence of solvents, CNCs can form chiral nematic mesophases, which can in turn be transferred to the solid state after evaporation. The resultant chiral nematic nanostructures (Figure 1b)^{9,10} can be distinguished by their in-plane property isotropy and iridescent structural coloration (Figure 1c).^{11,12}

Although the CNC chiral nematic organization can act at long-range and so serve as a structural template for other

material types assembly,^{13,14} external forces (e.g., shear, electric, magnetic, etc.) can disrupt the organization in order to align the CNCs in specific directions and obtain different material responses. For instance, shear-alignment of aqueous CNC suspensions has been previously explored to reduce the coefficient of thermal expansion of nanostructured CNC films, while maintaining film transparency¹¹ (Figure 1d); such tendency is highly beneficial in the design of organic electronic devices, especially light emitting diodes.^{2,4} Thermal conductivity is also a critical property, where CNC orientation can be very advantageous to improve heat management and offer a more efficient integral performance (i.e., device stability and durability²). Nonetheless, any structural modification performed to enhance optical and thermomechanical properties will be inherently connected to changes in the films’ heat transport properties. It is therefore desirable to understand the potential interplay between thermal conductivity and CNC organization, enabling further heat control in nanostructured materials.^{15,16}

Here, we combine molecular dynamics (MD) simulations with experimental measurements to achieve a multiscale description of the thermal conductivity from single cellulose

Received: August 2, 2014

Revised: September 24, 2014

Published: October 6, 2014

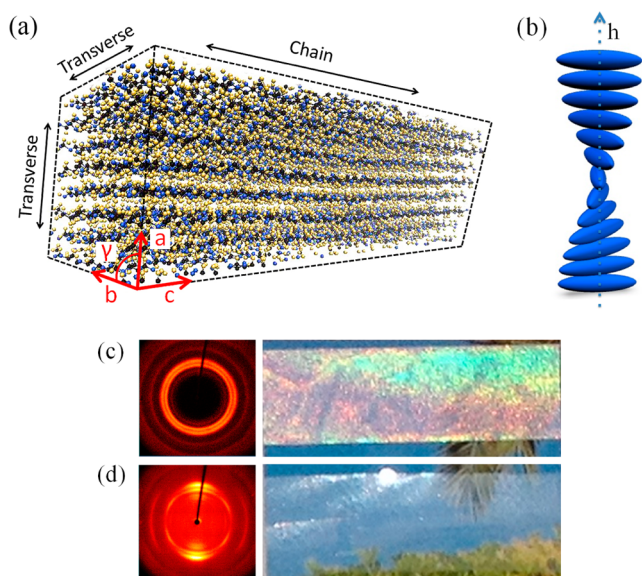


Figure 1. (a) Atomistic illustration of a monoclinic single cellulose $I\beta$ nanocrystal employed in MD simulations; spheres represent atoms with black carbon, blue oxygen, and yellow hydrogen. (b) Chiral nematic organization of individual CNCs following the helical direction (h), half pitch shown. Photographs of ~ 3 cm long, iridescent chiral nematic (c) and transparent shear oriented (d) cellulose nanostructured films. Insets in c and d show the typical 2D-XRD responses in transmission mode.

crystals to their organized nanostructured films having different degrees of CNC orientation, while highlighting the fundamental role played by CNC–CNC interfaces in the in-plane heat transport toward an integral design of nanostructured materials.

EXPERIMENTAL METHODS

CNC Film Preparation and CNC Alignment Characterization.

Self-organized films exhibiting the typical iridescent reflection and isotropic 2D-XRD response (Figure 1c) were prepared by slowly evaporating diluted aqueous CNC suspensions under ambient conditions. Shear-oriented films were obtained by shear casting concentrated, pH adjusted CNC suspensions under different shear rates (Table S1) followed by undisturbed ambient evaporation to lock in the CNC alignment within the film (Figure 1d). Increasing the shear rate increased the degree of CNC in-plane alignment. Further details regarding film fabrication can be obtained in our previous work.¹¹ To estimate the average CNC in-plane alignment within the bulk films, the Hermans order parameter¹⁷ (S) was calculated by integrating the intensity of the (200) crystalline plane as a function of the azimuthal angle using the 2D-XRD signals obtained for all films in transmission mode (equations S1–S3). In films with $S = 0$ there is no preferential in-plane CNC alignment, whereas $S = 1$ suggests perfect CNC alignment.

MD Simulations. Models of cellulose $I\beta$ crystals were constructed using Materials Studio software with unit cell parameters from X-ray diffraction¹⁸ and simulations were performed using LAMMPS simulation software.¹⁹ Three different systems were modeled (see Figures 1 and 2): a single crystal ($3.65 \times 3.36 \times 10.80$ nm³) and two adjacent crystals (each crystal $3.65 \times 3.36 \times 5.40$ nm³) aligned in three different orientations. Atoms at the two ends of both single-crystal and two-crystal systems were treated as rigid bodies. First, the temperature of the model system was set to 300 K and the structures were allowed to relax. Then, a constant heat flux was applied to the atoms adjacent to one of the rigid bodies and extracted at the other end. Simulations were run long enough to ensure the temperature distribution along the crystal or crystals was stable, ignoring phonon scattering effects. Thermal conductivity of the system was calculated using Fourier's law

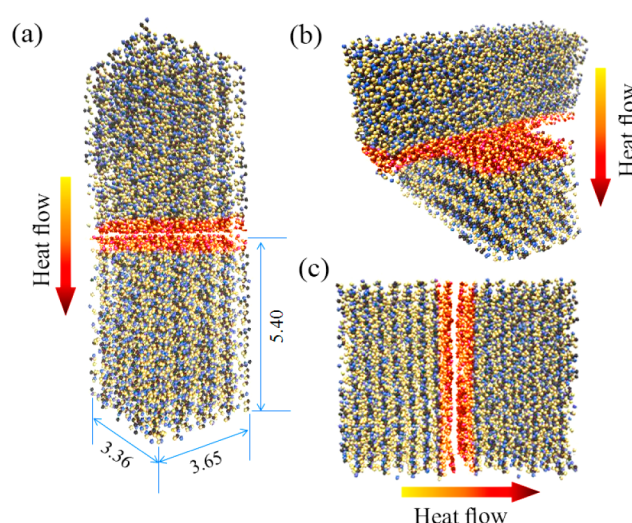


Figure 2. Atomistic model configurations studied for interfacial thermal resistance: (a) chain, (b) transverse perpendicular, and (c) transverse parallel; color scheme same as in Figure 1a with the interface regions highlighted in red.

based on the slope of the linear temperature distribution and the imposed heat flux; changing the heat flux by a factor of 10 resulted in a relatively small change (6%) in thermal conductivity. Four independent simulations were run for each case; values of thermal conductivity and associated error reported are the average and standard deviation from the four simulations. Other details about the cellulose $I\beta$ model used here can be found in our previous work.¹¹

Thermal Conductivity Measurement. The in-plane thermal conductivity (k) of the CNC films near room temperature were measured using a steady state bridge method with an aluminum radiation shield and vacuum enclosure setup that minimized radiative and convective heat losses, <6% total. Rectangular sections (25 mm $\times$ 3 mm) were first cut from the CNC film under study either perpendicular or parallel to the direction of crystal alignment. These sections were then stacked together and mounted within the measurement setup (see Figure S1) by attaching the longer (25 mm) edges to two suspended four-probe resistance thermometers of the same 25 mm length using thermal epoxy. The number of sections comprising the sample stack varied between one and four depending on the amount of parent material available, with a larger number of sections generally desirable so as to maximize signal strength versus background while maintaining a measurable temperature difference across the sample. The thickness of the parent material was measured with a precision micrometer and digital calipers prior to cutting and the total thickness of the stack taken as the average parent material thickness multiplied by the number of stacked sections. The parent material thickness values ranged from 0.030 mm for the thinnest material to 0.186 mm for the thickest. No interface material was used between stacked sections; however, care was taken during preparation to keep stacked components in close contact. In addition, the application of a vacuum prior to and during measurement combined with the flexible nature of the material facilitates the removal and closing of any air gaps that might still be present after sample mounting. By these means, any errors associated with interlayer gaps are minimized and expected to be negligible. The resistance thermometers and their supporting leads were all made of the same thin stainless steel wire (0.25 mm diameter). Prior to measurement, an aluminum radiation shield was placed around the sample/thermometer area (not shown in Figure S1) and the small vacuum enclosure was evacuated to about 10^{-1} Torr to minimize convection heat loss. A known DC heating current was then passed through the outer two probes of one resistance thermometer (heater line) while a much smaller sensing current was used for the opposing resistance thermometer (sensor line). The inner probes of each were used to

measure the voltage drop across the thermometer sections. The change in four-probe electrical resistance with temperature for the thermometers was determined beforehand by placing each on a heated platform with integrated thermocouple and varying the temperature. Thus, by monitoring the change in four-probe electrical resistance for each thermometer section during the measurement the average temperature rise of the heater line and sensor line can be determined, respectively. Combined with the known amounts of Joule heat being dissipated in the thermometer region and leads of the heating line, these temperatures allow for the in-plane thermal conductance and, hence, in-plane k of the film sample to be determined via conduction analysis of the setup's thermal circuit (see Supporting Information for further experimental details).

RESULTS AND DISCUSSION

Thermal Conductivity of Single CNCs. In order to estimate the individual contributions of single crystals to the thermal conductivity of a bulk film, we calculated the thermal conductivity of a single cellulose I β crystal using MD simulations (Figure 1a). Although electrons are not included in the model, we assume predictions are reasonable since electronic contributions to thermal conductivity are small in electrically insulating materials.^{16,20} Thermal conductivities in the chain (c -axis) and transverse (a - and b -axes) directions were obtained from the slope of the linear temperature distribution and the imposed heat flux by using Fourier's law.

The thermal conductivity in the chain direction was predicted to be $\sim 5.7 \pm 0.9 \text{ W m}^{-1} \text{ K}^{-1}$, whereas the transverse directions exhibited lower values $\sim 0.72 \pm 0.12 \text{ W m}^{-1} \text{ K}^{-1}$. The 10-fold increase in the chain direction can be directly correlated to the intrinsic crystalline anisotropy, where weaker intermolecular interactions in the transverse directions¹⁸ (i.e., hydrogen bonding in transverse directions as compared to covalent in the axial direction) can reduce phonon propagation. Materials with small unit cells, low thermal expansion, and average sound velocity ($\sim$ high elastic modulus to density ratio) are expected to have high thermal conductivity at high temperatures (i.e., above Debye temperature).²¹ Except for their relatively large²² unit cells, $\sim 0.658 \text{ nm}^3$,¹⁸ these properties are exhibited by the chain direction of a single cellulose I β crystal,^{6,11} therefore, yielding a thermal conductivity that is almost five times larger than that previously reported for cellulose fiber/epoxy composites in the in-plane direction² ($\sim 1.1 \text{ W m}^{-1} \text{ K}^{-1}$) and close to an order of magnitude larger than that exhibited by lingo-cellulosic specimens²³ (birch hardwood $\sim 0.25 \text{ W m}^{-1} \text{ K}^{-1}$) and by other types of materials like amorphous polymers^{24,25} $\sim 0.2 \text{ W m}^{-1} \text{ K}^{-1}$, as well as liquid crystal composites $\sim 0.7 \text{ W m}^{-1} \text{ K}^{-1}$ ²⁶ at room temperature.

Phonon Mean Free Path in Single CNCs. The range of phonon relaxation times and average phonon mean free paths for a single cellulose I β crystal in the transverse (~ 0.3 – 2.1 ps and ~ 1.7 – 5.3 nm) and axial directions (~ 0.6 – 1.5 ps and ~ 6.5 – 12.6 nm) were roughly estimated (eq S4) assuming that the heat transport is carried out only by acoustic phonons (i.e., electronic contribution to heat transport is minimal in electrically insulating materials and although heteroatom unit cells allow the presence of optical phonons, they contribute slightly to the transport of heat due to low group velocities²²). The approximated phonon mean free paths found in CNCs, keeping in mind that phonon mean free paths exhibit broad distributions,²⁵ were on the same order of magnitude as that calculated for highly aligned polyethylene,^{24,25,27} higher than that reported for vitreous silica above 200 K $\sim 7 \text{ \AA}$,²⁴ but lower than that calculated for a nanotube rope, $\sim 1 \text{ }\mu\text{m}$ at 30 K .²⁸

Phonon–phonon scattering supporting diffusive thermal equilibrium can be expected in the axial direction, as the phonon mean free path is shorter than the average longitudinal length of a single CNC, ~ 50 – 500 nm . More interesting, the fact that the phonon mean free path can exceed the lateral dimensions of single crystals of cellulose I β ~ 5 – 20 nm ,⁶ suggests that phonon scattering at interfaces can play a significant role in limiting the thermal conductivity in the bulk films.²⁹ The study of phonon scattering at interfaces offer unique opportunities for controlling bulk thermal conductivity as in the case of enhanced thermoelectric materials³⁰ (e.g., small grain size in polycrystalline systems).³¹ We propose an approach to capture this phenomenon in CNC nanostructured bulk films by estimating the interfacial thermal resistance or Kapitza resistance³² between two single cellulose I β crystals using MD simulations, and connecting it to phenomenological models to predict the bulk CNC response.

CNC–CNC Interfacial Thermal Resistance. We modeled the heat transport between two adjacent cellulose I β crystals in chain, parallel and perpendicular configurations (Figure 2), multiple interfacial configurations may be present during the self-organization of two identical crystals (e.g., 21 nonrepetitive configurations for six crystalline planes following Euler–Maclaurin sum formula with $f(n) = n$, $n = 6$), following the same procedure implemented in the analysis of a single crystal, and assuming serial thermal resistance across the two cellulose I β crystals and the interface between them, where the interface is modeled as an arbitrary object exhibiting the average properties between two identical crystals. Thus, the overall response follows,

$$\frac{L_t}{k_t A} = \frac{L_{c1}}{k_{c1} A} + \frac{L_i}{k_i A} + \frac{L_{c2}}{k_{c2} A} \quad (1)$$

where, L_t is the total length of the two CNC model, L_{c1} and L_{c2} are the lengths of each cellulose crystal, and L_i is the length of the interface in the heat transfer direction. A similar naming scheme is used for thermal conductivity, k . The cross-sectional area, A , is perpendicular to the direction of heat transfer and is constant for a given configuration (Figure 2). k_i in the chain configuration (Figure 2a) was $0.043 \text{ W m}^{-1} \text{ K}^{-1}$, calculated from eq 1 by using $L_{c1} = L_{c2} = 5.4 \text{ nm}$ as the lengths of the model crystals, $L_i = 0.44 \text{ nm}$, estimated for all configurations to be the average distance between two crystals,³³ and thermal conductivities $k_{c1} = k_{c2} = 5.7 \text{ W m}^{-1} \text{ K}^{-1}$ and $k_t = 0.77 \text{ W m}^{-1} \text{ K}^{-1}$ calculated from slope of the linear temperature distribution and the imposed heat flux as described previously. Using the same approach, k_i for the parallel (Figure 2b) and perpendicular (Figure 2c) configurations were estimated around 0.045 and $0.033 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. All results are summarized in Table S2.

The thermal conductivity calculated through the modeled interface was approximately 1 order of magnitude smaller than the total thermal conductivity of the two cellulose crystals in all three configurations, which supports the idea that heat transport in the bulk CNC films is limited by the interfaces between crystals. Interestingly, the range of thermal resistances estimated for the modeled interfaces between two cellulose I β single crystals (L_i/k_i), 9.4 to $12.6 \text{ m}^2 \text{ K GW}^{-1}$, was lower than that found in some low thermal conductivity thermoelectric alloys³⁴ (e.g., $\sim 95 \text{ m}^2 \text{ K GW}^{-1}$ for $\text{Si}_{0.7}\text{Ge}_{0.3}$ at 300 K) and even than that of materials governed by weak van der Waals interactions³⁵ but exceptionally high thermal conductivity

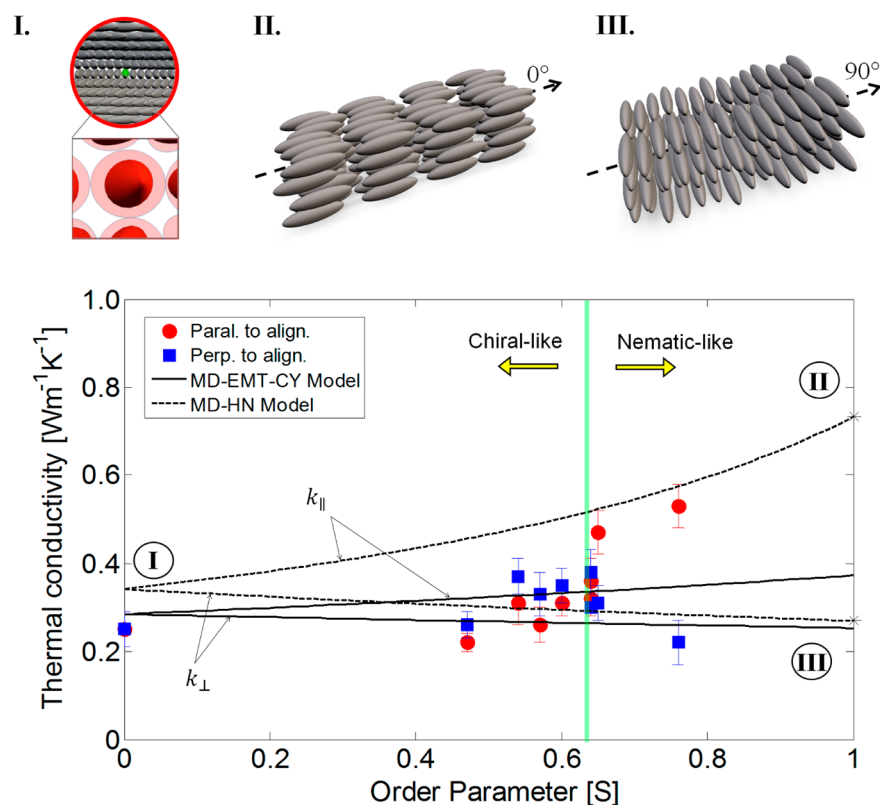


Figure 3. Experimental thermal conductivity of CNC films and model predictions as a function of orientation. (I) Isotropic chiral nematic organization in CNC films, half pitch shown. MD-EMT-CY model in CNCs assuming single crystals embedded in a chiral nematic matrix. Hypothetical $S \approx 1$ where CNCs are aligned parallel (II) and perpendicular (III) to the shear direction (MD-HN model). Bar at $S \approx 0.63$ represents a possible change in the global thermal conductivity behavior, in which the CNC chiral twisting is less predominant.

($\sim 6.6 \text{ kW m}^{-1} \text{K}^{-1}$)³⁶ like carbon nanotubes $\sim 83 \text{ m}^2 \text{K GW}^{-1}$. The lower interfacial thermal resistance estimated between cellulose crystals can be mainly attributed to their strong surface energy (i.e., van der Waals forces, hydrogen bonds, hydrophobic interactions^{37,38}), as thermal conductivity across interfaces scales with interfacial bonding strength.^{39–41} Further steps in enhancing heat transport in CNC bulk films could be achieved by controlling bonding at crystal–crystal interfaces together with the self-organization of single crystals.

Thermal Conductivity of CNC Films. We explored experimentally the thermal conductivity of freestanding CNC bulk films that were processed under two different conditions: self-organization and shear-orientation. Self-organized films exhibited iridescence and had a $S \approx 0.0$, which is consistent with the typical cholesteric orientations reported for such films.^{9–11} In contrast for the shear-oriented films, S ranged from ~ 0.47 to ~ 0.76 . The in-plane thermal conductivity for self-organized and shear-oriented CNC films is shown in Figure 3. Self-organized films exhibited in-plane isotropy ($0.25 \pm 0.04 \text{ W m}^{-1} \text{K}^{-1}$ at $S \approx 0$) likely due to the cholesteric organization present such films.^{9,10} For the shear-oriented films, the thermal conductivity was measured in the directions parallel ($k_{\parallel}$), and perpendicular ($k_{\perp}$) to the shear direction as a function of CNC alignment. With increased CNC alignment the thermal conductivity in the direction parallel to shear direction increased, where at $S \approx 0.76$ there was a 2-fold increase $\sim 0.53 \pm 0.05 \text{ W m}^{-1} \text{K}^{-1}$ as compared to self-organized films. For the direction perpendicular to the shear direction, the thermal conductivity slightly increased at low orientations as CNC alignment increased, likely due to an improvement of

phonon propagation due to the random interfacial contacts, followed by a decrease at high orientations (above $S \approx 0.63$), consistent with the increase of interfaces in the heat flow direction (Figure 3III). The overall effect of increasing anisotropy in the thermal conductivity as molecular alignment increases has been also observed in liquid crystals,^{42,43} polymers,⁴⁴ and biomacromolecules⁴⁵ in which molecular interactions are typically mediated by strong directional hydrogen bonds. (Figure 4, Table S2). Figure 4 also shows how CNC-based materials offer a broad spectrum of design possibilities as CNC alignment can provide low coefficients of thermal expansion, as compared to graphene composites, while controlling thermal conductivity and optical response. Likewise, factors such as thermally activated intercrystalline motion,¹¹ crystal–crystal interfaces and crystal alignment tend to modify the thermal expansion and thermal conductivity of bulk cellulose $I\beta$ films as compared to single cellulose $I\beta$ crystals in their correspondent directions, yet providing similar responses (Figure 4).

Modeling Thermal Transport in Nanostructured CNC Films. The connection between the thermal conductivity of a single cellulose $I\beta$ crystal and the experimental thermal conductivity of bulk films can be established by integrating the critical role of interfacial thermal resistance⁴⁶ with elements like single crystal anisotropy and CNC orientation within a multiscale predictive model. Here, we employ two different models to describe the chiral nematic-like and nematic-like response of CNC films based on MD predictions. Such an approach can be directly extended to other complex nanostructured materials,¹⁶ polycrystalline structures,³⁴ and compo-

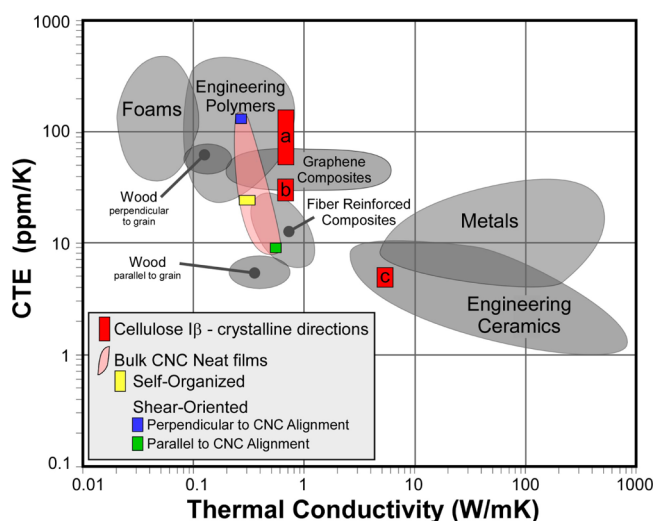


Figure 4. Ashby plot of thermal response of cellulose I β and bulk CNC films with respect to other engineering materials. Results for cellulose I β and bulk CNC films were based on the MD simulations and experimental measurements, respectively.

site systems³⁵ where interfaces and organization are governing factors.

Since the in-plane isotropic response observed in self-organized CNC films is given by a highly organized chiral nematic structure with a finite number of interactions rather than by a random distribution,¹¹ we approximate the description of the system as an effective medium and account for the distribution of orientations following Choy and Young's adaptation⁴⁷ of Maxwell's effective medium theory (EMT-CY) and the Hermans order parameter (eqs S2–S4). The EMT-CY model has been previously applied to describe the thermal conductivity response in oriented semicrystalline polymers^{27,47,48} as the traditional EMT assumptions (i.e., anisotropic, noninteracting spherical inclusions embedded in continuous medium) could be approximated to crystals embedded in an amorphous polymeric matrix. A similar approach is adopted here, in which we consider an interface, as modeled in CNC–CNC Interfacial Thermal Resistance, and an anisotropic single crystal as a composite unit cell⁴⁶ expanding throughout the film (Figure 3I), as given by eqs S5–S9. The scheme agrees with the initial deduction of an inclusion interacting with the average medium as a whole⁴⁷ instead of dealing with a multibody interaction and allows the estimation of thermal conductivity in CNC films by using MD simulations as the only input parameters.

Figure 3 shows how the MD-EMT-CY model approaches the thermal conductivity of films tested in the direction parallel to shear direction ($k_{\parallel}$) as single CNCs align along the shear direction. Although capturing the slight decrease present in the experimental data, thermal conductivities in the direction perpendicular to shear orientation ($k_{\perp}$) were underestimated, as the model does not account for possible additional phonon contributions. A more accurate phenomenological description can be based on the film processing conditions and crystal characteristics, involving possible medium discontinuities, crystalline size distribution, and account for any potential interaction or spacing generated by electrolytes present in the precursor suspensions. Although, some of the micromechanical (e.g., Halpin–Tsai, percolation, etc.), and classical EMT models could address a few of those effects separately,^{46,49–51} the

simple MD-EMT-CY approach can closely bound the thermal conductivity response of CNC films, suggesting that for low alignments (i.e., below $S \approx 0.63$) the nanostructured films will tend to transport heat in the in-plane direction like a chiral nematic composite structure (Figure 3I) rather than as a disorganized system. However, such a generalized approach (Figure 3I) would be less applicable once the chiral nematic structure is less predominant (i.e., in Figure 3 MD-EMT-CY model saturates around $S \approx 0.63$) and nanostructured films can be better seen as CNC clusters pointing out at a specific angle with respect to the shear direction (Figure 3, cases II and III), therefore, approaching Henning's (HN) proposed treatment.⁵²

In Henning's model (eqns S10–S12), tensor transformations are employed to account for the influence of orientation and properties of structural units in the properties of the bulk films.⁵² The model, that is in principle based on rotational symmetric crystals, has also predicted the response of uniaxially stretched amorphous polymers.⁵² Although a parallel configuration can also be conceived (i.e., assuming a uniform temperature gradient),²⁴ a series model assuming uniform heat flux throughout the structure and summing up thermal resistivities has been shown to describe well the thermal conductivity of films in the directions parallel and perpendicular to shear direction.⁵² The MD-HN model predicts a thermal conductivity of $\sim 0.35 \text{ W m}^{-1} \text{ K}^{-1}$ for an isotropic film, which is close to that found by MD-EMT-CY $\sim 0.29 \text{ W m}^{-1} \text{ K}^{-1}$, which, in turn, is closer to that of the self-organized films ($\sim 0.25 \pm 0.04 \text{ W m}^{-1} \text{ K}^{-1}$) due to the cholesteric structural assumption. Thus, the MD-HN model can also describe more accurately the thermal conductivity of CNC films above $S \approx 0.63$ as compared to the MD-ECM-CY model, likely due to the fact that the effect that inherent polydispersity of CNCs has on thermal conductivity of bulk films can be reduced in the HN model as considering crystalline clusters and interfacial contacts are unbalanced along the film, being minimized parallel and maximized perpendicular to shear alignment.

CONCLUSIONS

We described via MD simulations how the intrinsic anisotropy of single cellulose crystals produced a thermal conductivity in the chain direction that is ten times greater than that estimated in the transverse directions (Table S2, Figure 4). Using an order of magnitude analysis we determined that the phonon mean free path can actually exceed the dimensions of the single crystal, suggesting a significant contribution of interfaces to phonon scattering. MD simulations confirmed a drastic decrease in thermal conductivity due to the interface between two cellulose crystals in several different configurations. Nonetheless, such inherent thermal transport barrier found for CNCs was almost an order of magnitude lower than that exhibited by carbon nanotubes and equal to those present in low thermal conductivity thermoelectric alloys. Two models –MD-EMT-CY and MD-HN– that account for CNC orientation and CNC–CNC interfaces captured the experimental in-plane thermal conductivity response of bulk CNC films. We also demonstrated how MD simulations and CNC orientation can closely describe and potentially control the conductive heat transport from nanostructured isotropic-cholesteric to anisotropic shear-oriented cellulose films, while keeping an intricate connection with the broad range of possible optical responses needed for further material usage in current and future cost-effective, technological applications.

■ ASSOCIATED CONTENT

■ Supporting Information

Table with experimental conditions employed during film processing (i.e., shear rates, CNC wt % in aqueous suspensions). Table summarizing thermal conductivities found experimentally and by MD simulations for both single crystals and bulk CNC films, along with other reference materials. Hermans order parameter with related equations of tested CNC films. Additional information regarding phonon mean free path approximations and thermal conductivity measurements. Equations for MD-EMT-CY and MD-HN models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jpyoungb@purdue.edu.

*E-mail: dboday@us.ibm.com.

*E-mail: amartini@ucmerced.edu.

*E-mail: robertmoon@fs.fed.us.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the Air Force Office of Scientific Research Grant #FA9550-11-1-0162 for supporting this project.

■ REFERENCES

- (1) Nogi, M.; Iwamoto, S.; Nakagaito, A. N.; Yano, H. *Adv. Mater.* **2009**, *21*, 1595–1598.
- (2) Shimazaki, Y.; Miyazaki, Y.; Takezawa, Y.; Nogi, M.; Abe, K.; Ifuku, S.; Yano, H.; Chemical, H. *Biomacromolecules* **2007**, *8*, 2976–2978.
- (3) Nogi, M.; Yano, H. *Adv. Mater.* **2008**, *20*, 1849–1852.
- (4) Chen, L.-F.; Huang, Z.-H.; Liang, H.-W.; Guan, Q.-F.; Yu, S.-H. *Adv. Mater.* **2013**, *25*, 4746–4752.
- (5) Kuczynski, J.; Boday, D. J. *Int. J. Sustain. Dev. World Ecol.* **2012**, *19*, 557–563.
- (6) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. P. *Chem. Soc. Rev.* **2011**, *40*, 3941–3994.
- (7) Zhou, Y.; Fuentes-Hernandez, C.; Khan, T. M.; Liu, J.-C.; Hsu, J.; Shim, J. W.; Dindar, A.; Youngblood, J. P.; Moon, R. J.; Kippelen, B. *Sci. Rep.* **2013**, *3*, 24–26.
- (8) Habibi, Y.; Lucia, L. A.; Rojas, O. J. *Chem. Rev.* **2010**, *110*, 3479–3500.
- (9) Vignolini, S.; Rudall, P. J.; Rowland, A. V.; Reed, A.; Moyroud, E.; Faden, R. B.; Baumberg, J. J.; Glover, B. J.; Steiner, U. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 15712–15715.
- (10) Majoinen, J.; Kontturi, E.; Ikkala, O.; Gray, D. G. *Cellulose* **2012**, *19*, 1599–1605.
- (11) Diaz, J. A.; Wu, X.; Martini, A.; Youngblood, J. P.; Moon, R. J. *Biomacromolecules* **2013**, *14*, 2900–2908.
- (12) Müller, M.; Zentel, R.; Keller, H. *Adv. Mater.* **1997**, *9*, 159–162.
- (13) Caruso, R.; Schattka, J. *Adv. Mater.* **2000**, *12*, 1921–1923.
- (14) Shopsowitz, K. E.; Qi, H.; Hamad, W. Y.; MacLachlan, M. J. *Nature* **2010**, *468*, 422–425.
- (15) Pernot, G.; Stoffel, M.; Savic, I.; Pezzoli, F.; Chen, P.; Savelli, G.; Jacquot, A.; Schumann, J.; Denker, U.; Mönch, L.; Deneke, C.; Schmidt, O. G.; Rampnoux, J. M.; Wang, S.; Plissonnier, M.; Rastelli, A.; Dilhaire, S.; Mingo, N. *Nat. Mater.* **2010**, *9*, 491–495.
- (16) Cahill, D. G.; Ford, W. K.; Goodson, K. E.; Mahan, G. D.; Majumdar, A.; Maris, H. J.; Merlin, R.; Phillpot, S. R. *J. Appl. Phys.* **2003**, *93*, 793.
- (17) Hermans, J. J.; Hermans, P. H.; Vermaas, D.; Weidinger, A. *Recl. Trav. Chim. Pays-Bas* **1946**, *65*, 427–447.
- (18) Nishiyama, Y.; Langan, P.; Chanzy, H. *J. Am. Chem. Soc.* **2002**, *124*, 9074–9082.
- (19) Plimpton, S. J. *Comput. Phys.* **1995**, *117*, 1–42.
- (20) Privalko, V.; Novikov, V. *Adv. Polym. Sci.* **1995**, *119*, 1–77.
- (21) Pietralla, M. J. *Comput. Mater. Des.* **1996**, *3*, 273–280.
- (22) Toberer, E. S.; May, A. F.; Snyder, G. J. *Chem. Mater.* **2010**, *22*, 624–634.
- (23) Suleiman, B. M.; Larfeldt, J.; Leckner, B.; Gustavsson, M. *Wood Sci. Technol.* **1999**, *33*, 465–473.
- (24) Choy, C. *Polymer* **1977**, *18*, 984–1004.
- (25) Wang, X.; Ho, V.; Segalman, R. A.; Cahill, D. G. *Macromolecules* **2013**, *46*, 4937–4943.
- (26) Akatsuka, M.; Takezawa, Y. *J. Appl. Polym. Sci.* **2003**, *89*, 2464–2467.
- (27) Choy, C.; Luk, W.; Chen, F. *Polymer* **1978**, *19*, 155–162.
- (28) Hone, J.; Whitney, M.; Piskoti, C.; Zettl, A. *Phys. Rev. B* **1999**, *59*, R2514–R2516.
- (29) Minnich, A. J.; Dresselhaus, M. S.; Ren, Z. F.; Chen, G. *Energy Environ. Sci.* **2009**, *2*, 466.
- (30) Snyder, G. J.; Toberer, E. S. *Nat. Mater.* **2008**, *7*, 105–114.
- (31) Feser, J. P.; Chan, E. M.; Majumdar, A.; Segalman, R. A.; Urban, J. J. *Nano Lett.* **2013**, *13*, 2122–2127.
- (32) Kapitza, P. *Phys. Rev.* **1941**, *60*, 354–355.
- (33) Wu, X.; Moon, R. J.; Martini, A. *Tribol. Lett.* **2013**, *52*, 395–405.
- (34) Nan, C.-W.; Birringer, R. *Phys. Rev. B* **1998**, *57*, 8264–8268.
- (35) Huxtable, S. T.; Cahill, D. G.; Shenogin, S.; Xue, L.; Ozisik, R.; Barone, P.; Usrey, M.; Strano, M. S.; Siddons, G.; Shim, M.; Keblinski, P. *Nat. Mater.* **2003**, *2*, 731–734.
- (36) Berber, S.; Kwon, Y.; Tomanek, D. *Phys. Rev. Lett.* **2000**, *1*–4.
- (37) Glasser, W. G.; Atalla, R. H.; Blackwell, J.; Malcolm Brown, R.; Burchard, W.; French, A. D.; Klemm, D. O.; Nishiyama, Y. *Cellulose* **2012**, *19*, 589–598.
- (38) Sacui, I. A.; Nieuwendaal, R. C.; Burnett, D. J.; Stranick, S. J.; Jorfi, M.; Weder, C.; Foster, E. J.; Olsson, R. T.; Gilman, J. W. *ACS Appl. Mater. Interfaces* **2014**, *6*, 6127–6138.
- (39) Hu, M.; Shenogin, S.; Keblinski, P. *Appl. Phys. Lett.* **2007**, *91*, 241910.
- (40) Hu, M.; Keblinski, P.; Schelling, P. *Phys. Rev. B* **2009**, *79*, 104305.
- (41) Losego, M. D.; Moh, L.; Arpin, K. A.; Cahill, D. G.; Braun, P. V. *Appl. Phys. Lett.* **2010**, *97*, 011908.
- (42) Kato, T.; Nagahara, T.; Agari, Y.; Ochi, M. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 3591–3599.
- (43) Kato, T.; Nagahara, T. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1419–1425.
- (44) Choy, C.; Kwok, K. J. *J. Appl. Polym. Sci., Part B: Polym. Phys.* **1999**, *32*, 1389–1397.
- (45) Huang, X.; Liu, G.; Wang, X. *Adv. Mater.* **2012**, *24*, 1482–1486.
- (46) Nan, C.-W.; Birringer, R.; Clarke, D. R.; Gleiter, H. *J. Appl. Phys.* **1997**, *81*, 6692–6699.
- (47) Choy, C.; Young, K. *Polymer* **1977**, *18*, 769–776.
- (48) Choy, C.; Chen, F.; Luk, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1187–1207.
- (49) Lee, J.-H.; Lee, S.-H.; Choi, C. J.; Jang, S. P.; Choi, S. U. S. *Int. J. Micro-Nano Scale Transp.* **2010**, *1*, 269–322.
- (50) Hamilton, R.; Crosser, O. *Ind. Eng. Chem. Fundam.* **1962**, *1*, 187–191.
- (51) Progelhof, R. *Polym. Eng. Sci.* **1976**, *16*, 615–625.
- (52) Henning, J. J. *J. Polym. Sci., Part C: Polym. Symp.* **1967**, *16*, 2751–2761.