Tunable thermal switching via DNA-based nano-devices

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Abstract
DNA has a well-defined structural transition—the denaturation of its double-stranded form into two single strands—that strongly affects its thermal transport properties. We show that, according to a widely implemented model for DNA denaturation, one can engineer DNA ‘heattronics’ devices that have a rapidly increasing thermal conductance over a narrow temperature range across the denaturation transition (∼350 K). The origin of this rapid increase of conductance, or ‘switching’, is the softening of the lattice and suppression of nonlinear effects as the temperature crosses the transition temperature and DNA denatures. Most importantly, we demonstrate that DNA nano-junctions have a broad range of thermal tunability by varying the sequence and length, and exploiting the underlying nonlinear behavior. We discuss the role of disorder in the base sequence, as well as the relation to genomic DNA. These results set the basis for developing thermal devices out of materials with nonlinear structural dynamics, as well as understanding the underlying mechanisms of DNA denaturation.

Online supplementary data available from stacks.iop.org/Nano/24/095704/mmedia
(Some figures may appear in colour only in the online journal)

1. Introduction
Thermal transport in nanoscale materials and molecules has enormous potential in developing devices that manage heat in electronic and other systems [1]. For instance, thermal rectifiers [2, 3], thermal transistors [4], tunable thermal links [5] and thermal memory [6, 7] have been experimentally demonstrated (for a recent review see [8]). One can envision that many more such devices will become feasible as methods are developed to engineer and control nonlinear effects in materials that transport heat.

Nature has provided us with a versatile and diverse nonlinear structure: DNA. The structural dynamics of DNA are fundamentally interesting due to their relevance in biological processes, such as transcription [9] and replication [10]. Further, DNA is also being used in constructing functional nanoscale devices, such as a template for electronic devices [11] and molecular motors [12]. Thus, its ability to transport heat under different conditions is technologically important and may allow the ‘DNA template’ to be exploited not just as a scaffold but also as a functional device in itself. In addition to theoretical predictions [13], a recent experiment has shown that incorporation of DNA into a device can indeed give rise to nonlinear behavior in the thermal current [14]. The experimental setup examines a change in the thermal conductance from a combined duplex DNA and fluid conductor to a disordered single-stranded DNA layer, the latter being thermally insulating compared to the former. A complete theoretical reconstruction of the experimental results would thus need to delineate the role of DNA’s intrinsic thermal conductance from the surrounding
media, and examine a disordered layer of single-stranded DNA.

In this work, however, we envision instead a single molecule of duplex DNA bridging two thermal reservoirs in a water vapor atmosphere. Such an environment is essential for our purposes since: (i) it suppresses solvent-mediated leakage heat currents between the reservoirs, and yet (ii) the vapor atmosphere has been shown to preserve the natural behavior of DNA (e.g. denaturation) [15]. We demonstrate that in this setup one can tune the thermal transport properties of DNA by taking advantage of its function as the carrier of the genetic code via its sequence of the four bases—adenine (A), guanine (G), cytosine (C), thymine (T). The sequence of bases determines both local structural properties that influence the thermal conductance and also where nonlinear effects give way to denaturation. Together with the length of the DNA strand, these characteristics make DNA’s thermal transport properties highly tunable. Based on this behavior, we predict that a DNA-based nano-device can act as a thermal switch: the thermal conductance can rise rapidly by many orders of magnitude as the temperature of the DNA strand is driven across the denaturation transition. Thus, the proposed device can switch between ‘off’ (i.e. heat-insulating) and ‘on’ (i.e. heat-conducting) states. This is the ‘heatronic’ analog of an electronic switch [11]. Further, we illustrate the ‘engineering principles’ behind tuning thermal transport, which will be broadly applicable to nonlinear materials and help set the foundations for developing novel thermal devices for applications in, for example, nanoscale electronics.

2. Theoretical analysis

Our starting point is the Peyrard–Bishop–Dauxois (PBD) model [16–18], which considers double-stranded DNA as a one-dimensional lattice of nonlinear oscillators. This model—the common model for the dynamics of DNA denaturation—captures the essential statistical features of DNA’s structural transition and allows for the direct calculation of nonequilibrium thermal transport properties [13] (see figure 1). Within the PBD model, the DNA is described by the Hamiltonian

\[ H = \sum_n \left[ \frac{m_n \dot{y}_n^2}{2} + V_n(y_n) + W_n(y_n, y_{n-1}) \right], \]

where each base pair (bp) of mass \( m_n \) is represented by stretching of its hydrogen bonds via the coordinate \( y_n \). The onsite and nearest-neighbor interaction potentials, \( V_n \) and \( W_n \), depend on the sequence of bases. The potentials take on the form \( V_n(y_n) = D^2(e^{-\alpha y_n} - 1)^2 \) (known as the Morse potential), which describes hydrogen bonding and effective interactions due to the backbone/environment, and

\[ W_n(y_n, y_{n-1}) = \frac{K_n}{2} (1 + \rho_n e^{-\beta_n(y_n+y_{n-1})})(y_n - y_{n-1})^2, \]

where \( \alpha \) and \( \beta_n \) are the thermal conductance ratio

\[ R = \frac{\kappa_H}{\kappa_L}, \]

which describes the stacking interaction between neighboring base pairs. The scenario of interest is a DNA strand in a water vapor atmosphere similar to recent experiments [15], where it was shown that the PBD model still describes the transition well6. For the analytical results, we consider a uniform stacking parameter, and then we address sequence-dependent stacking using numerical simulations (see [19, 20], and the supplemental data for a detailed derivation and numerical parameters available at stacks.iop.org/Nano/24/095704/mmedia). We designate the sequence of DNA by the series of bases in one of the strands (in the 3′-to-5′ direction). The sequence of the other strand is unambiguously determined by requiring the DNA duplex to be 100% complementary. Thus, only DNA double strands with no mismatches are dealt with in this work.

We will first focus on the thermal conductance ratio

\[ R = \frac{\kappa_H}{\kappa_L}, \]

where \( \kappa_H(1) \) is the thermal conductance at low (high) temperatures. This quantity was introduced in [13] as a way to characterize the heat transport properties of a material near its thermally induced structural transition. Here we will examine its sequence dependence. When calculated using a small temperature change, e.g. around the denaturation temperature, it can play the role of an ‘on–off’ ratio. We will see that adjusting the sequence and length of the DNA can tune \( R \) while the sequence alone allows the transition temperature to be tuned within certain limits.

One of the main principles behind the nonlinear behavior predicted by the PBD model is captured in the low (L) and

5 We note that other theoretical works have examined thermal transport in models of DNA [30–32]. However, these have not examined the strong nonlinear effects during denaturation, which is our focus here and in [13].

6 In fact, the PBD model, or a PBD-like model, may be applicable even in a vacuum, as it was shown that the DNA duplex can retain some of its structural properties under extreme conditions [33].
These limits have the form of the end sites, the thermal conductance of an infinite strand in stranded to single-stranded forms. With reservoirs attached on within the PBD model—of DNA going from its double-stranded to its high (H) temperature limits of equation (1):

$$H_\mu = \sum_n \left[ \frac{m_n y_n^2}{2} + D_{\mu n}^2 + \frac{K_{\mu n}^n}{2}(y_n - y_{n-1})^2 \right].$$

where $\mu = L, H$. We note that the PBD model is an effective model of DNA near the denaturation transition. However, these limiting forms that occur at much higher/lower temperatures give the appropriate physical description—within the PBD model—of DNA going from its double-stranded to single-stranded forms. With reservoirs attached on the end sites, the thermal conductance of an infinite strand in these limits has the form

$$\kappa = \frac{J}{T_H - T_L} = \int \omega \omega W(D_{\mu n}^n, K_{\mu n}^n, m, \gamma, \omega),$$

which can be calculated analytically (see [21, 22, 13] and the supplemental data available at stacks.iop.org/Nano/24/095704/mmedia). Here, $J$ is the heat current, the integration is over the frequencies that correspond to propagating modes ($\omega$), $\gamma$ characterizes the coupling strength to the reservoirs, and the transmission function $\omega$ is determined by the structure of the lattice.

Figure 2(a) shows $\kappa_L(H)$ and $R$ for an infinite strand with several different motifs, i.e. the basic unit cells of the DNA lattice. The high temperature conductance of all the sequences is identical due to the uniform stacking interaction. The low temperature conductance, however, varies tremendously as the motif is changed and is universally much lower than its high temperature counterpart. This behavior is driven by two distinct physical mechanisms. First, going from the low temperature form to the high temperature form results in the release of the onsite confining potential upon denaturation. This leads to softening of the phonon modes and consequently to the increase of the thermal conductance, as described analytically in [13]. Second, the introduction of different motifs creates a non-uniform lattice (due to the different binding potentials of the AT and GC pairs). This results in a narrowing and splitting of the phonon bands, as shown in figure 2(b), and a subsequent reduction in the low temperature thermal conductance. In the extreme case of a semi-infinite poly(A) strand connected to a semi-infinite poly(G) strand the non-uniformity would have maximal effect: the phonon bands would have no overlap (see figure 2(b)) and the strand as a whole would have zero heat conductance within this model.

Actual DNA, though, will have other contributions to heat conduction (e.g. the backbone), which will lead to a non-zero conductance.

A natural question to ask is what is the heat conductance of genomic or random sequences? Studying strands with periodic motifs helps us understand the behavior of random sequences. An infinite random sequence—and likely genomic sequences—will look like a periodic strand with an extremely long motif. The allowed bandwidth of propagating modes will be narrowed by the large number of sites in the motif. Thus, we do not expect heat to be conducted efficiently and the low temperature $\kappa$ should be very small for random sequences (compared to a uniform sequence or an alternating sequence). Genomic DNA, of course, is always finite and not completely random. We expect, however, that the result will be similar to that of a

Figure 2. Engineering the thermal conductance of DNA. (a) The thermal conductance ratio and conductance for infinite strands with different periodic motifs computed analytically from the high/low temperature limits of the PBD model. The low temperature conductance (blue circles), $\kappa_L$, drops precipitously as the motif of the sequence is enlarged while the high temperature conductance (red squares), $\kappa_H$, stays the same. The thermal conductance ratio, $R$, introduced in [13], is the ratio of the high to low temperature thermal conductance and characterizes how DNA's thermal conductance changes as it denatures. (b) Analytically calculated phonon bands, from the lattice parameters used to fit the PBD model to experimental denaturation curves, for selected DNA sequences at low temperature. The left-most bands are for a homogeneous sequence of G (upper, purple band) and a homogeneous sequence of A (lower, green band). As the motif is enlarged, the bands will become narrower and also split. In other words, periodic sequences with increasing lengths of periodicity will decrease the bandwidth of the phonon modes, drastically reducing DNA's ability to conduct heat at low temperature. Although some bands have relatively small widths on the plot, all bands have finite widths.
random sequence. However, small regions of the genome can look very different from a random sequence, and nature may exploit sequence variation to optimize heat (signal) transport.

3. Numerical results and discussions

The PBD model was developed to describe the properties of DNA around the denaturation transition. The analytical results above addressed high and low temperature limits (within the simplification of uniform stacking interactions). In order to understand the extent to which the values of $R$ realized in figure 2(a) can be realized in a narrow temperature range around a transition, we perform numerical simulations of the full model including a sequence-dependent stacking interaction (parametrized in [20]). The heat current is obtained by keeping the temperature difference between the heat baths constant ($T_H - T_L = 10$ K) and scanning the average temperature $\langle T \rangle = (T_H + T_L)/2$. We consider 90 base pair (bp) long strands with 20 bp at each end connected to Langevin reservoirs. The damping of the individual sites by the reservoirs is 0.5 ps$^{-1}$. This is large enough to keep the very ends at the temperature of the reservoirs, while still allowing the sites to fluctuate at their natural frequency. The supplemental data (available at stacks.iop.org/Nano/24/095704/mmedia) has further details on the numerical simulations.

Figure 3(a) shows the heat current for several sequences. The analytical results above predicted that the heat conductance at temperatures higher than the melting temperature is insensitive to a particular sequence since the stacking interaction was assumed uniform. This is not the case in the numerical simulations, where the stacking potential assumes a more realistic sequence-dependent form. Accordingly, the heat current exhibits a dependence (although rather weak) on sequence in the temperature range 400–450 K. However, the heat conductance of DNA increases drastically when the temperature increases across the denaturation point. That this is indeed the denaturation transition where the conduction of the DNA strand changes rapidly (versus temperature) can be seen by the correspondence between these curves and the peaks in the heat capacity shown in figure 3(b). Around the transition, poly(AG) and poly(A$_2$G$_2$) have about the same conductance and heat capacity, implying that the denaturation bubbles—where the two strands locally come apart—are much longer than the motif and, thus, only the average sequence matters. Thus, the sequence can be used to tune the ‘operating temperature’ of the device via its effect on the denaturation temperature. The GC base pair has a higher dissociation energy than AT, and thus its incorporation into a strand increases the transition temperature.

Furthermore, while the sequence can change the ‘operating’ temperature and the thermal conductance ratio, $R$, measured by the high/low temperature limits, the on–off ratio around the ‘operating’ temperature, for example just below to just above the transition, is due to a more complex set of factors than just $R$. However, tuning the length of the DNA nano-junction allows one to directly tune this important device characteristic. Figure 4(a) shows the heat conductance of poly(A) strands of various lengths. Below the transition, the strand is anharmonic and is expected to demonstrate finite well-defined conductivity, i.e. the conductance is expected to be inversely proportional to the length of the strand so long as this length is longer than the typical bubble size. As seen in figure 4(a), near (and above) the transition, the conductance weakly depends on the length, signifying that the harmonic, high temperature Hamiltonian is being approached. This is further supported by figure 4(b), where above the transition point the heat capacity is seen to rapidly approach $C/k_B = 1$—the harmonic limit.
Figure 4. Engineering the range of operation using the length of DNA. (a) Numerically calculated heat conductance of poly(A) of length 50, 100 and 200 bps (with an additional 20 bp segment connected to a reservoir at each end). (b) Numerically calculated heat capacity around the denaturation temperature for poly(A) of varying lengths.

At temperatures further below the transition, the conductance drops inversely with length of the DNA within the error of the simulations. This observation is in agreement with the heat capacity which shows the transition narrowing for longer strands of DNA. This is simply an indication that when the bubble length becomes comparable to the strand length denaturation has effectively occurred. This finite size effect broadens the transition in temperature. We conjecture that using sequence effects (e.g. the suppression of the low temperature conductance shown in figure 2(a)) together with length will allow for even more drastic on–off jumps in the thermal conductance. However, a more detailed study of DNA, including backbone effects, will be required to investigate this issue.

We note that, right at the transition, the shorter DNA actually has lower conductance. This is probably due to the effect of the ‘clamped’ ends, which make anharmonic effects more important for the shorter strands due to keeping the bases at the ends in the bound state.

4. Conclusion

To summarize, we have examined the thermal transport properties of DNA as described by the PBD model. We predict that a DNA-based nano-device can act as a thermal switch due to its rapidly rising thermal conductance as the temperature of the DNA strand is driven across the denaturation transition. The operating principle behind this behavior is the release of the base pairs from their confining potential, which both softens the lattice and suppresses nonlinear effects as the temperature is increased through the transition. Using analytical calculations and numerical simulations with sequence-specific parameters, we have shown that the operating temperature of the thermal switch can be tuned by choosing different DNA motifs and that the ‘on/off’ ratio can be tuned by the DNA length. Our suggested experiments are well within current experimental reach, and recent advances in the measurement of the thermal conductance in various nano-junctions composed of, for example, carbon nanotubes [23], Si nanowires [24–26] and especially individual DNA–gold complexes [27], give potential routes to realizing the setup we propose.

Further possibilities for engineering thermal transport may be offered by molecular or chemical modification of the nucleotides, using much longer sequences (see, for example, the inset of figure 3(b), showing that a two-step jump in conductance may be possible), and exploiting extrinsic changes in heat conduction (for example, due to a structural change modifying the surrounding environment in addition to changing intrinsic properties, as in a recent experiment [14]). This work sets the foundation to developing thermal switches out of materials and molecules with nonlinear structural dynamics. In addition, it will allow one to test underlying mechanisms for structural transitions [13] and, in particular, the dynamical behavior captured within the PBD model [13, 28, 29]. We speculate that biological systems may take advantage of such nonlinear behavior in engineering their own control of heat flows and signaling.

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