Electronic Specific Heat of DNA: Effects of backbones and disorder

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In this present work we report the results of our investigation on the electronic specific heat of the DNA molecule within tight-binding framework by using the dangling backbone ladder model. We have studied both electronic specific heat and density of states in order to supplement our results. We take four different DNA sequences namely poly(dA)-poly(dT), poly(dG)-poly(dC), Random ATGC and a Fibonacci sequence, where the first two are periodic, third one is random and the last one is a quasi-periodic sequence (where A is adenine, T is thymine, G is guanine, and C is cytosine). The roles of backbone structure and the environmental effects on the electronic specific heat are discussed. We observe that irrespective of the sequences we have taken there is a universal response of the electronic specific heat for both the clean case and even in presence of environmental fluctuations. The nature of response of specific heat on backbone disorder is totally opposite in the low and high temperature regime.

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I. INTRODUCTION

Since the last decade, interest in studying the electrical properties of DNA has enhanced considerably, as it shows that it can conduct electrons, it becomes a promising agent for future nano electronic devices which can help to overcome the drawbacks like energy efficiency of present silicon-based devices. Not only this, it has many advantageous properties like self-assemble and self-replication which can make it possible to produce nanostructures with greater precision that is not achievable with classical silicon-based technology [1]. It is also quite smaller in size and may be the best nanowire at present. The question whether DNA or in broad aspect biomolecules can conduct electrons or not, started dates back to 1962, when Eley and Spivey [2] first suggested that DNA could behave like an electrical conductor. The first effort to use organic molecules as electrical components started quite early in 1974 [3], but the lack of knowledge of electrical properties of DNA made it difficult. With time, the advent of new-generation sophisticated techniques and low temperature measurement facilities make it possible to investigate the physical properties of DNA and other biomolecules. Till date a large number of studies have been performed on electronic transport properties of DNA. A various number of different techniques have been applied which include measurements on single-stranded DNA [4, 5], measurements on oriented DNA strands on lipid films [6], measurement on the current-voltage (I-V) characteristics of unordered DNA on the nanocontacts [7, 8], and also on artificially made poly(GC) chains [9]. Despite these vast efforts no conclusive results appear, on contrary DNA behaves in different modes in electrical conduction, such as an insulator [10], wide-band gap semiconductor [5], ohmic [9], and even proximity-induced superconductor at low temperature [11]. This large variety of experimental results led to various theoretical models in which charge transport is mediated via polarons [12], solitons [13], electrons and holes [14-15]. Thus electronic transport properties of DNA still remain quite debatable and controversial and Ref. [17] provides a vivid review.

While there is so much effort to understand the electrical properties of DNA, there is mere number of attempts have been made to study its thermal and thermodynamic properties [16-24]. Recently in a study [22] it has been shown that knowledge of thermal properties, like specific heat and others, may be useful to characterize different neurodegenerative diseases like Alzheimer and Parkinson. In our work we would like to extend the knowledge of thermal properties of DNA specially specific heat further in view of potential application. Our main aim is to investigate the role of backbones in different electronic specific heat (ESH) spectra, seeking possible differences and similarities among them, with the purpose to establish some kind of standard behavior. We model DNA within tight-binding framework incorporating its backbone structure which was lacking in the previous studies [18-21, 23-24], to investigate the effect of the presence of backbones and also of the environment. We use four DNA sequences ranging from periodic, quasi-periodic to random, and see that irrespective of sequences there is a uniform response of specific heat in clean case (no disorder) and even in presence of environmental effects.

This paper is organized as follows. In Sec. II we introduce the model Hamiltonian and briefly discuss about our theoretical formulation. We analyze our numerical results in Sec. III and finally conclude in Sec. IV.

II. MODEL AND THEORETICAL FORMULATION

To study the ESH spectra of DNA molecule we use the so called dangling backbone ladder model (DBLM)
within tight-binding framework \[25, 26\], as it is more appropriate to use than the simple ladder model \[21\] since it incorporates the backbone structure of DNA. As the sugar-phosphate backbones are negatively charged and hanging outside the double-helix structure of DNA, they can easily interact with the substrate and the effective on-site energies of the backbone get modulated to a great extent \[10, 11, 27, 31\] introducing disorder into the system as a measure of environmental fluctuations and we can study the environmental effects using this model.

The effect of environment on the thermal properties of DNA, specially on the specific heat is so far not-well explored and for this purpose we use the following tight-binding Hamiltonian (DBLM) to mimic DNA molecule (see Fig. 1)

![Diagram of DNA molecule](image)

**FIG. 1:** (Color online) Schematic view of the dangling backbone ladder model to study ESH spectra of double-stranded DNA. The red (thick) and blue (thin) lines are the two strands and the large solid dots on them are the nucleotides. The small black dots on the upper and lower sides of the ladder represent the backbones and the dotted lines between two types of dots represent the coupling between the nucleotides with corresponding backbone sites.

The binding Hamiltonian (DBLM) to mimic DNA molecule explored and for this purpose we use the following tight-can study the environmental effects using this model.

\[
H_{DNA} = H_{ladder} + H_{backbone} \, ,
\]

where,

\[
H_{ladder} = \sum_{i=1}^{N} \sum_{j=1,II} \left( \epsilon_{ij} c_{ij}^\dagger c_{ij} + t_{ij} c_{ij}^\dagger c_{i+1,j} + \text{H.c.} \right) + \sum_{i=1}^{N} v \left( c_{II}^\dagger c_{II} + \text{H.c.} \right) \, ,
\]

\[
H_{backbone} = \sum_{i=1}^{N} \sum_{j=1,II} \left( \epsilon_i^{q(j)} c_{i,q(j)}^\dagger c_{i,q(j)} + t_i^{q(j)} c_{i,q(j)}^\dagger c_{i,q(j)} + \text{H.c.} \right) \, ,
\]

where \( c_{ij}^\dagger \) and \( c_{ij} \) are the creation and annihilation operators for electrons in the \( i \)th Wannier state, \( t_{ij} \) = intrastrand hopping integral between neighboring nucleotides along each strand of the ladder, \( \epsilon_{ij} \) = on-site potential energy of the nucleotides, \( t_i^{q(j)} \) = hopping amplitude between a nucleotide and the corresponding backbone site, \( \epsilon_i^{q(j)} \) = on-site potential energy of the backbone sites with \( q(j) = \uparrow, \downarrow \) for \( j=I \) and II respectively denoting upper and lower backbone sites, \( v \) = interstrand hopping integral between two neighboring sites of DNA in two different strands (we call it vertical hopping). For simplicity we set \( \epsilon_i^{q(j)} = \epsilon_b \) and \( t_{ij} = t_i \) and \( t_i^{q(j)} = t_b \).

To study the electronic specific heat of the DNA molecule we use the most general formalism where the specific heat at constant volume is given by the partial derivative of the average energy of the system with respect to the temperature

\[
C_v = \frac{\partial < E >}{\partial T} \, (4)
\]

where,

\[
< E > = \sum_{i=1}^{N} (E_i - \mu)f(E_i) \, (5)
\]

\[
f(E_i) = \frac{1}{1 + \exp(\frac{E_i - \mu}{k_B T})} \, (6)
\]

where \( < E > \) is the average energy of the system, \( E_i \) the energy of an electron at \( i \)th eigenstate, \( \mu \) is the chemical potential, \( T \) is the temperature, \( k_B \) is the Boltzmann constant and \( f(E_i) \) is the occupation probability according to Fermi-Dirac statistics for each energy state with energy \( E_i \). Using the expressions of \( < E > \) and \( f(E_i) \) we find the following expression for electronic specific heat (ESH) of DNA

\[
C_v = \sum_{i=1}^{N} \frac{(E_i - \mu)^2 \exp(\frac{E_i - \mu}{k_B T})}{k_B T^2(\exp(\frac{E_i - \mu}{k_B T}) + 1)^2} \, (7)
\]

To explain the ESH spectra we also study the electronic density of states (DOS) of the system. We use green’s function formalism to find DOS of the system which is given by

\[
\rho(E) = -\frac{1}{\pi} \text{Im}[\text{Tr}[G(E)]] \, (8)
\]

where, \( G(E) = (E - H + i\eta)^{-1} \) is the green’s function for the entire DNA molecule with electron energy \( E \) where \( \eta \rightarrow 0^+ \), \( H \) = Hamiltonian of the DNA and Im and Tr represents imaginary part and trace over the entire Hilbert space respectively.

### III. RESULTS AND DISCUSSIONS

To study the ESH of DNA, we take four different DNA sequences, two of them are periodic, one is random and another is quasi-periodic Fibonacci sequence which is derived using following inflation rule : \( A \rightarrow AT, T \rightarrow A \). We first study the effect of backbone environment, by using two different models, simple ladder model and dangling backbone ladder model, where the later one incorporates the backbone structure. Afterwards we use only DBLM
to find the environmental effects, introducing disorder into the system via backbones. To represent the actual experimental situation, we simulate these environmental fluctuations in our model by considering the backbone site-energy $\bar{\epsilon}_b$ to be randomly distributed within the range $[\bar{\epsilon}_b-w/2, \bar{\epsilon}_b+w/2]$, where $\bar{\epsilon}_b$ represents the average backbone site-energy and $w$ is the disorder strength. We have also investigated the DOS for the four different DNA sequences as stated earlier for different disorder strength ($w$). For numerical investigation the on-site potential energies of the nucleotides ($\epsilon_{ij}$) are taken as the ionization potential potential and the following numerical values are used through out the present work: $\epsilon_C = 8.177$ eV, $\epsilon_C = 9.722$ eV, $\epsilon_A = 8.631$ eV, $\epsilon_T = 9.464$ eV. The intrastand hopping integral between like nucleotides are taken as $t=0.35$ eV while between unlike nucleotides are taken as $t=0.17$ eV. We take interstrand hopping parameter i.e., vertical hopping to be $v=0.3$ eV. The parameters used here are extracted from the \textit{ab-initio} calculations \cite{32–34}. Now as all the nucleobases are connected with the sugar-phosphate backbone by identical C-N bonds, the corresponding hopping integral between the nucleobases and backbone sites is taken to be equal for all the cases and we set $t_b=0.7$ eV \cite{31,55}. We also set $k_B=1$.

FIG. 2: (Color online) a. Electronic specific heat ($C_v$) vs temperature (T) plot with and without backbones (no sequence, all site-energies are set to zero). $C_v$ increases as we introduce backbones into the system except at low temperature (see inset). b. Density of states (DOS) vs. energy (E) with and without backbones. It is clearly visible that due to introduction of backbones a gap opens in the system.

In Fig. 2 we show the behavior of specific heat ($C_v$) with temperature (T) for a general ladder model in comparison with DBLM where the later one incorporates the backbone structure of the DNA. For both the models we set the site-energies of the ladder and backbone sites to zero. It is clear from the figure that due to insertion of the backbone $C_v$ gets increased for most of the temperature scale, except the low-temperature regime. The corresponding DOS profiles are also shown alongside.

First let us explain the basic nature of the $C_v$ vs temperature (T) curve. At low temperature only the states within range of $E_F \pm kT$ are only accessible, where $E_F$ being the Fermi energy. Now average energy of the system is given by $<E>_T = \int E \rho(E) f(E) dE$, at low temperature we can make the following approximations: $dE = kT$, $\rho(E) \approx \rho = $ a constant, if $(E) \approx 1$, then average energy becomes $<E>_T \approx \rho k^2 T^2$. Then specific heat becomes $C_v = \rho k^2 T$, proportional to the temperature, so $C_v$ will increase with temperature at low temperature. Now this DNA system is a finite one, so the band-width is also finite and at high temperature all the states are accessible. Now as we increase the temperature in the high temperature regime there is no new excited states to access, so specific heat decreases with temperature and it will go to zero at very high temperature.

Following the same argument we can explain the behavior of the result of Fig. 2. There is a gap in the system due to presence of the backbones, as we increase temperature at low temperature range, there is no states to access, so the $<E>_T$ of the system can’t increase as it can for the general ladder model (without backbone) since it has no gap in the system. So, at low temperature regime $C_v$ decreases due to introduction of backbones. Now, at high temperature, as thermal energy become comparable to the energy gap of the system, the excited states of the DBLM become accessible despite of the energy gap. As the excited states of DBLM has higher energy than that of the general ladder model, so $<E>_T$ will increase with much higher rate at high temperature and accordingly $C_v$ will increase due to presence of backbones.

FIG. 3: (Color online) Electronic specific heat ($C_v$) as a function of backbone disorder strength ($w$) for four different DNA sequences at low temperature (T<2K). $C_v$ decreases with disorder ($w$) except initial rise at low w for all the cases.

In Fig. 3 we plot the variation of specific heat with
FIG. 4: (Color online). Density of states (DOS) profiles for four DNA sequences at different disorder strength (w). a’s are poly(dA)-poly(dT), b's are poly(dG)-poly(dC), c’s are random ATGC and d’s are Fibonacci sequences.
backbone disorder for low temperature (T<2K). It is clear from the figure that $C_v$ increases first at low disorder
then it decreases monotonically as disorder increases.

The reason is clear from the DOS profiles provided in
Fig. 4. At zero disorder ($w$) there is gap in the system
for all the sequences, for small $w$ new states are
started to come around the Fermi energy ($E_F$) and the
gap started to vanish. These new states can be accessed
at low temperature, so at low disorder $C_v$ increases.
For large disorder the gap is totally vanished, and the band
starts to expand around the edges, there are new excited
states coming out around the band-edges at the
cost of the states around the $E_F$ (band-center) as the
total number of states are fixed for the system. So, the
DOS falls around $E_F$, hence $C_v$ decreases (at low tem-
perature $C_v \propto \rho$).

In Fig. 5 we show the same variation of $C_v$ with back-
bone disorder strength ($w$) for high temperature (T>2K) range, and it shows that $C_v$ increases with temperature.
To explain these we once again look at the correspond-
ing DOS profile Fig. 4. At the high temperature all the
states are accessible, now as we increase disorder, there
are new states are coming around the band-edges and the
energy of these states also increase with $w$. As these
states has high energy cost, the rate of change of average
energy $<E>$ gets increased with increasing $w$, so $C_v$
also increases.

In Fig. 6 we show the variation of $C_v$ with tempera-
ture ($T$) for four DNA sequences at different backbone
disorder strength ($w$). In all the plots $C_v$ decreases at
low temperature and increases at high temperature with
increasing $w$, as discussed earlier. The new thing is, the
peak value of $C_v$, which determines the crossover temper-
ature, also decreases with disorder as this falls within the
low temperature range. There is also some fluctuations in
$C_v$ at low temperature under appreciable disorder ($w$>5).

Earlier oscillatory behavior of ESH was reported by E. L.
Albuquerque et. al. [24], at low temperature for quasi-
periodic sequences only; here we get same kind of fluctu-
ations for all the sequences at low temperature but under
environmental effects.

In Fig. 7 we show the dependence of crossover temper-
ate ($T_c$) with backbone disorder strength ($w$). Except the Fi-
onacci one the nature of variation is almost same for all the
sequences.

In Fig. 4 we show the dependence of crossover temper-
ate ($T_c$) (i.e., at this temperature $C_v$ becomes maxi-
mum) on backbone disorder ($w$). It shows that $T_c$
increases monotonically with $w$, though the rate of in-
crease is not uniform everywhere but the variation is al-
most same for different DNA sequences except for quasi-
periodic Fibonacci one. For Fibonacci sequence $T_c$
increases upto a certain disorder strength then it decreases.

**IV. CONCLUDING REMARKS**

Till date thermal properties of DNA and other
biomolecules are not yet well explored. We make an at-
tempt to examine the electronic specific heat response of
a DNA-like system by modelling it within tight-binding framework. Though there are some results are available in the literature on DNA specific heat, but they did not take into account the backbones as the model used by them do not consider this basic structure of the DNA molecule. So, we try to study the backbone effect and also the effect of the environment on the electronic specific heat of the DNA. It comes out that introduction of backbones makes changes in the DOS profile i.e., the band structure of the system by opening a gap in the central region of the band and due to this the specific heat gets increased all over the entire temperature range except in the low temperature regime. On environmental disorder, $C_v$ reacts in two different ways, at low temperature it decreases with backbone disorder strength ($w$) and at high temperature range it increases with $w$. Not only this, the cross-over temperature ($T_c$) which signifies the maximum value of specific heat also increases with disorder ($w$). We have been able to put forward a regularize behavior of ESH of DNA which is independent of the sequence we have chosen. The response of ESH is quite universal not only for the clean case ($w=0$) but also in presence of environmental effects, which implies that ESH of the system reacts to the environment in the same way irrespective of its sequential variety. Now for the application purpose, heat exchange in the process of protein binding, unfolding, ligand association and other bimolecular reactions can now be measured easily. There are three basic techniques used for this measurements, are the Differential scanning calorimetry (DSC), which measures sample heat capacity with respect to a reference as a function of temperature, Isothermal titration calorimetry (ITC), which measures the heat absorbed or rejected during a titration experiment and the third one is thermodynamic calorimetry (for a detail description see Ref. [30]). But unfortunately none of these techniques is able to separate the electronic contribution to the specific heat of biomolecules, as they measure all contributions including the vibrational ones. However, our results, theoretical predictions can be tested experimentally, at least in the low temperature range, with modifications of these tools in the near future. We hope that there will be experimental verification of our results and other investigations to find thermal properties of DNA and other biomolecules as it is happening regularly in case of electronic transport properties of the same.

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