Effect of thermal fluctuations of twist angles on charge transport in DNA: A model calculation

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We report theoretical investigations of charge transport through model DNA sequences with and without a superconducting electrode, focusing on the effect of the twist angle between neighboring base pairs which varies due to thermal fluctuations. The twist-angle fluctuation causes the averaged hopping matrix element to decrease and to fluctuate, leading to a significant thermal enhancement of charge transport at low temperatures. The Lyapunov exponent of the model DNA with a superconducting lead is twice that for normal leads due to Andréev reflection, and its temperature dependence is approximately independent of the sequence.

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Charge transfer through DNA sequences has been a subject of research for several decades since the original discussions by Ladik[1] and Eley and Splivey[2] in the 1960s. Such processes have been reported in recent photoexcitation measurements, which indicated long-range charge transfer through DNA molecules.[3] Since charge transfer appears to be possible from one part of DNA to other parts, extensive effort has been devoted to charge transport measurements through DNA where charge is injected into DNA through some external metal contacts.[4–14] Experimental data collected so far on charge transport through DNA have shown different and sometimes controversial results, ranging from proximity-induced superconductivity,[7] to a reasonably good conductor with a resistance of 2.5 MΩ,[5] to a semiconductor behavior with an energy gap of a few eV,[6,8] all the way to totally insulating behavior with bias voltage up to 10 *V*.[4,10,15,16] The wide range of transport behaviors can, perhaps, be attributed to many experimental complications in each measurement. These complications include chemical details of the environment, geometry and properties of the metal contacts, length and structure of the DNA during measurements, impurity, temperature, substrate, humidity, oxygen concentration, water solution, etc. Since many possibilities exist, an important theoretical task is to examine general features of charge transport through DNA as affected by various physical factors.

An interesting experimental study on transport through DNA has been the proximity effect induced by superconductivity.[7] By contacting a λ-DNA molecule with superconducting electrodes,[7] it is found that DNA molecules can conduct current down to millikelvin temperatures and phase coherence is maintained over several hundred nanometers. The behavior of hybrid superconducting systems is a very important topic in nanoelectronic device physics; it is useful and interesting to understand the peculiarities of DNA molecules contacted by superconductors. It is well known that at a normal conductor–superconductor (NS) interface, an incoming electronlike excitation can be reflected as a holelike excitation, the so-called Andréev reflection. This gives rise to a doubling of the conductance quanta, i.e., $G_{NS}=2G_N$ for hybrid quantum point contacts,[17] where $G_N \equiv 2e^2/h$ is the conductance quanta for normal conductors.

In this paper, we investigate the problem of how the Andréev reflection affects quantum transport through model DNA sequences. An ideal theoretical transport calculation should include superconducting electrodes, counterions, and other environmental factors in addition to the DNA molecule, and compute *nonequilibrium* charge distribution and current in an applied electric field self-consistently for a variety of device and environmental configurations. Such a calculation is clearly not possible even using supercomputers. On the other hand, many qualitative physics can already be inferred by using simple models parametrized by experimental or *ab initio* data. We employ such an analysis: here we focus on the qualitative and generic transport physics rather than quantitative details of the quantum chemistry. As such, our work can be viewed as a part of an effort to understand the general physics of charge transport in periodic and aperiodic DNA contacted by external leads.[1,4–14]

We calculate the transmission coefficient and other related quantities as a function of temperature, for various model DNA sequences in the presence of a superconducting electrode using a tight-binding atomic model.[13] Temperature causes thermal fluctuations which smear out quantum interference during charge transport, as well as other structural changes of the DNA. We focus on one of these structural changes, namely, the twist-angle fluctuations between base pairs. Within a tight-binding model, this effect enters into the model Hamiltonian through the hopping parameter. Due to this off-diagonal fluctuation, electrons are localized at high temperatures. When the hopping matrix element is varied due to temperature which in turn shifts resonant energy levels of the system, charge transport can be greatly enhanced at low temperatures. The charge transport under random fluctuation of the twist angle is characterized by a Lyapunov exponent γ; we calculate γ as a function of temperature T for both normal and NS systems involving different model DNA sequences: the poly(G)-poly(C) sequence, the Fibonacci poly-GC sequence, several λ-phage sequences, and the hu-

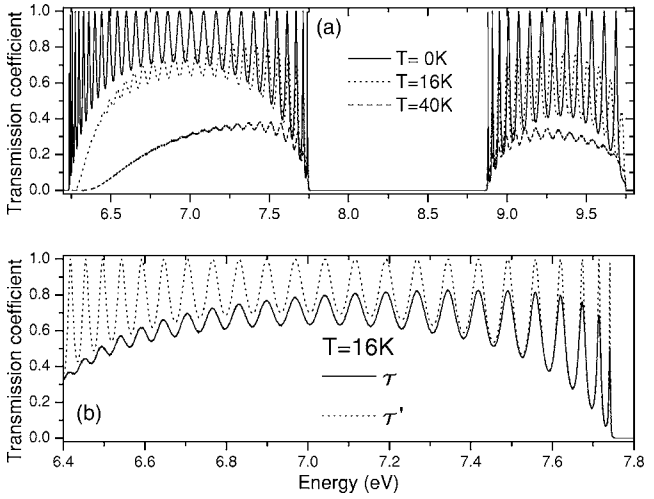

FIG. 1. (a) Transmission coefficient $\mathcal{T}$ of model poly(G)-poly(C) sequence versus energy at different temperatures. Here $t_{DNA}=1$ eV. (b) $\mathcal{T}$ and $\mathcal{T}'$ vs energy at $T=16$ K.

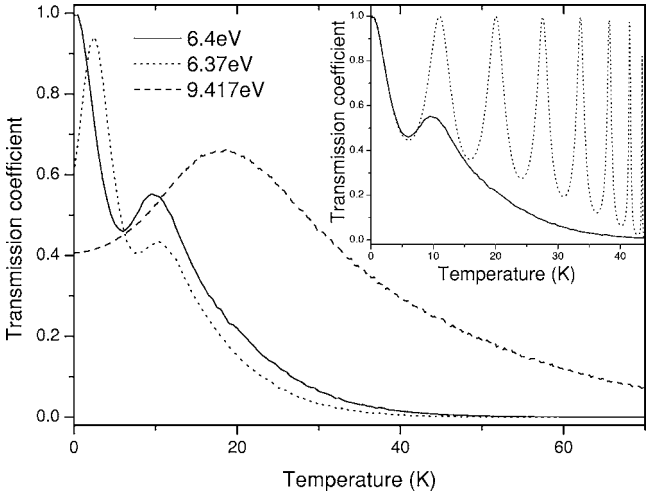

FIG. 2. $\mathcal{T}$ vs temperature at different energies. Inset: $\mathcal{T}$ (solid line) and $\mathcal{T}'$ vs temperature for $E=6.4$ eV.

man chromosome 22. We find that there exists an approximately *universal* functional form $\gamma=\gamma(T)$ which holds for the eight model DNA sequences we have studied. In the presence of a superconducting electrode, γ is found to be twice the value of normal electrodes due to Andréev reflection.

Our analysis proceeds as follows. We consider the following tight-binding Hamiltonian to describe the model DNA sequences:[11,13]

$$H=\sum_{l}\left[-t_{DNA}\cos(\theta_{l,l+1})(c_l^{\dagger}c_{l+1}+\text{H.c.})+\epsilon_l c_l^{\dagger}c_l\right] \quad (1)$$

where $c_l^{\dagger}$ is the creation operator for an electron at site l; ϵ_l is the on-site energy which depends on the details of the sequence; t_{DNA} is the hopping matrix element at zero temperature; and $\theta_{l,l+1}$ is the randomly fluctuating twist angle between neighboring base pairs. Here we assume that θ follows a Gaussian distribution such that $\langle\theta\rangle=0$ and $\langle\theta^2\rangle=kT/I\Omega^2$ from the equipartition theorem with $I\Omega/k=250$ K.[13] The on-site energies are chosen as $\epsilon_A=8.24$ eV, $\epsilon_T=9.14$ eV, $\epsilon_C=8.87$ eV, and $\epsilon_G=7.75$ eV following Ref. 18. The electrode is made of type-G nucleotide bases. Charge transport through NS structures is determined by the Andréev reflection coefficient $\mathcal{T}_A$,[17]

$$\mathcal{T}_A=2\mathcal{T}^2/(2-\mathcal{T})^2 \quad (2)$$

where $\mathcal{T}$ is the transmission coefficient of normal structures.

In the following calculation, we choose the hopping matrix between electrodes and the scattering region to be $t_d=1$ eV; other values t_d are also studied. In Fig. 1(a), we plot the transmission coefficient $\mathcal{T}$ of the poly(G)-poly(C) sequence as a function of the Fermi energy at three different temperatures $T=0$, 16, and 40 K (solid, dotted, and dashed lines, respectively). Since any measurement is carried out within a finite time interval which potentially samples many structure configurations, in the numerical calculation we have averaged over 10 000 configurations for each energy. In general, the temperature has two effects on the hopping matrix element t_{DNA}: the thermal fluctuation part that obeys a Gaussian distribution; and the variation of rms of the hopping matrix element due to change of temperature. Indeed, Fig. 1(a) shows these two effects on the transmission coefficient $\mathcal{T}$. (1) $\mathcal{T}$ has two envelopes[19] at zero temperature corresponding to the maxima and minima of $\mathcal{T}$ (solid line). Due to thermal fluctuations, quantum interference is partially destroyed and the magnitude of the envelopes in the transmission coefficient decreases (dotted and dashed lines). (2) Although thermal fluctuations destroy quantum interference, a thermal *enhancement* of conductance at low temperature is possible, due to a shift of resonance levels in the model DNA. From Fig. 1(a), comparing peak positions E_r of each curve, we observe that at a finite temperature E_r has a nonlinear shift from the center of the band gap (around $E_c=8.4$ eV). Roughly, E_r is shifted to $(E_r-E_c)t_T/t_{DNA}$, where $t_T\equiv t_{DNA}\cos(\sqrt{\langle\theta^2\rangle})$ is the rms hopping matrix element at temperature T (a similar shift is also seen in Fig. 2). Therefore, due to the shift of resonance positions, at a given energy E the transmission coefficient $\mathcal{T}(E)$ can vary from a minimum to a maximum when the temperature is varied—thus a thermal *enhancement* which is a drastic change of transport properties. To understand what physical factor causes this drastic effect, Fig. 1(b) plots $\mathcal{T}$ at temperature $T=16$ K (solid line) and the corresponding transmission coefficient $\mathcal{T}'$ (dotted line) which is obtained by neglecting the thermally fluctuating part of the hopping matrix element, i.e., replacing $t_{DNA}\cos\theta$ by t_T. The peaks of $\mathcal{T}$ and $\mathcal{T}'$ are aligned perfectly, allowing us to conclude that shifts of peak positions in Fig. 1(a) are solely due to variations of the rms hopping matrix elements. To understand this, we note that the rms hopping matrix element t_T at finite temperature is smaller than that of the zero-temperature t_{DNA} and hence the energy spectrum of the corresponding model DNA sequence is shifted. This in turn affects the resonant level of the model DNA sequence and its transmission coefficient. Since the resonant level is not very sensitive to on-site energy, the total energy scale of the transmission coefficient is scaled by a

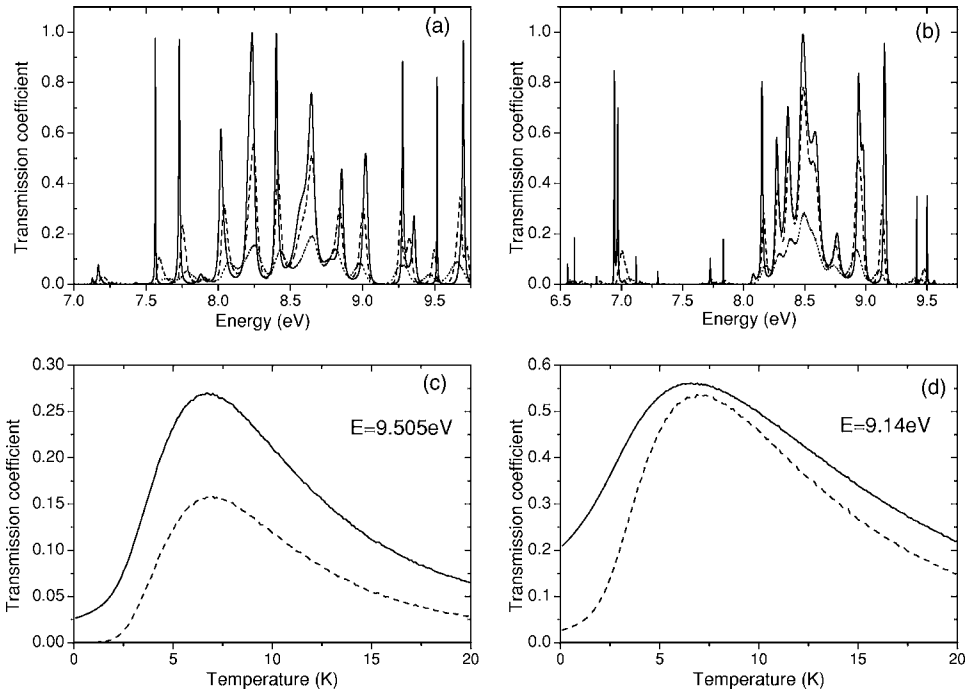

FIG. 3. $\mathcal{T}$ vs energy at different temperatures for (a) λ_2-DNA sequence and (b) the human chromosome 22. Solid line ($T=0$), dashed line ($T=16$ K), and dotted line ($T=40$ K). (c) and (d) $\mathcal{T}$ (solid line) and $\mathcal{T}_A$ vs temperature at fixed energies.

factor t_T/t_{DNA} from the kinetic term of the Hamiltonian. Hence we conclude that thermal fluctuations of the hopping matrix element destroy phase coherence while the change of the rms hopping matrix element shifts the resonant peaks.

Figure 2 plots the transmission coefficient $\mathcal{T}$ versus temperature for several energies. When energy is chosen at a resonance (solid line), $\mathcal{T}$ decreases as temperature increases. Near $T=10$ K there is a small peak indicating thermal enhancement due to the shift of resonant peaks as discussed above. The inset plots a comparison between $\mathcal{T}$ (solid line) and $\mathcal{T}'$ (neglecting thermal fluctuation) versus temperature at $E=6.4$ eV: there would be more peaks in transmission coefficients versus temperature if there were no thermal fluctuation. When the system is off resonance (dotted line in main panel of Fig. 2), $\mathcal{T}$ increases rapidly as temperature is turned on, and there are two peaks at $T=3$ and 10 K as a result of thermal-assisted transport. The thermal enhancement can also be observed at a higher temperature $T=20$ K (dashed line in Fig. 2).

Our numerical results indicate that thermal enhancement is a generic feature that exists in other model DNA sequences such as poly(G)-poly(C), Fibonacci poly-GC sequences, several λ phage sequences, and the human chromosome 22. Figures 3(a) and 3(b) plot the transmission coefficient $\mathcal{T}$ versus energy at different temperatures for λ_2-DNA and human chromosome 22 model sequences. We note that at zero temperature, the result agrees with that of Ref. 20. In Figs. 3(c) and 3(d), the enhancement of the transmission coefficient and Andréev transmission coefficient are displayed.

We have also investigated the temperature dependence of the Lyapunov exponents for different model DNA sequences. The Lyapunov exponent is defined as $\gamma=-\langle\ln[\mathcal{T}(E)]\rangle_E/2N$ where N is the number of sites in the DNA and $\langle\cdots\rangle_E$ is the average over the energy.[21] We found that at zero temperature the Lyapunov exponents of eight different types of DNA sequences, the poly(G)-poly(C) sequence, the Fibonacci poly-GC sequence, the λ_1 chain (the first 60 base pairs of the λ phage sequence), the λ_2 chain (the next 60 base pairs), λ_3, λ_4, and λ_5, and the human chromosome 22 are, respectively, $\gamma_i=0.086$, 0.073, 0.112, 0.114, 0.131, 0.083, 0.081, and 0.093. At finite temperatures, we can express the Lyapunov exponent as[11] $\gamma_i(T)=\gamma_i+\gamma(T)$ where $\gamma(T)$ is the temperature-dependent part. Our numerical results show that Lyapunov exponents of the above eight different types of DNA sequences have approximately the same temperature dependence [Fig. 4(b)], i.e., $\gamma(T)$ is approximately a universal function.

In the presence of a superconducting electrode, Andréev reflection can enhance or suppress charge transport depending on whether the system is near a resonance. Figure 4(a) depicts the Andréev reflection coefficient versus energy at different temperatures. We have the following observations. (1) At zero temperature, the resonant peak value reaches 2 instead of 1 as in the normal case [compare to Fig. 1(a)]. (2) The minima of the Andréev reflection coefficients decrease drastically. (3) Similar to Fig. 1, the resonant structure in Fig. 4(a) shows the same nonlinear shift giving rise to thermal enhancement of charge transport [see also Fig. 4(c)]. These features can be understood from Eq. (2) by which we observe that there is a value for the transmission coefficient $T=0.764$ above (below) which $\mathcal{T}_A$ [Eq. (2)] is enhanced (suppressed). In particular, when the system is very transmissive or near a resonance, i.e., when $\mathcal{T}\sim 1$, we have $\mathcal{T}_A\sim 2\mathcal{T}$. This is the well-known doubling effect due to Andréev reflection. However, when the system is off resonance or in the localization regime with very small transmission coefficient $\mathcal{T}\ll 1$, we have $\mathcal{T}_A\sim\mathcal{T}^2/2$ which is even smaller. Because of this feature, we have the relation $\gamma_{NS}=2\gamma_N$ in the large-N limit. Our numerical results on eight different model DNA sequences confirm this result at finite temperatures below the superconducting transition. Figure 4(c) shows the transmission coefficient versus temperature for the poly(G)-poly(C)

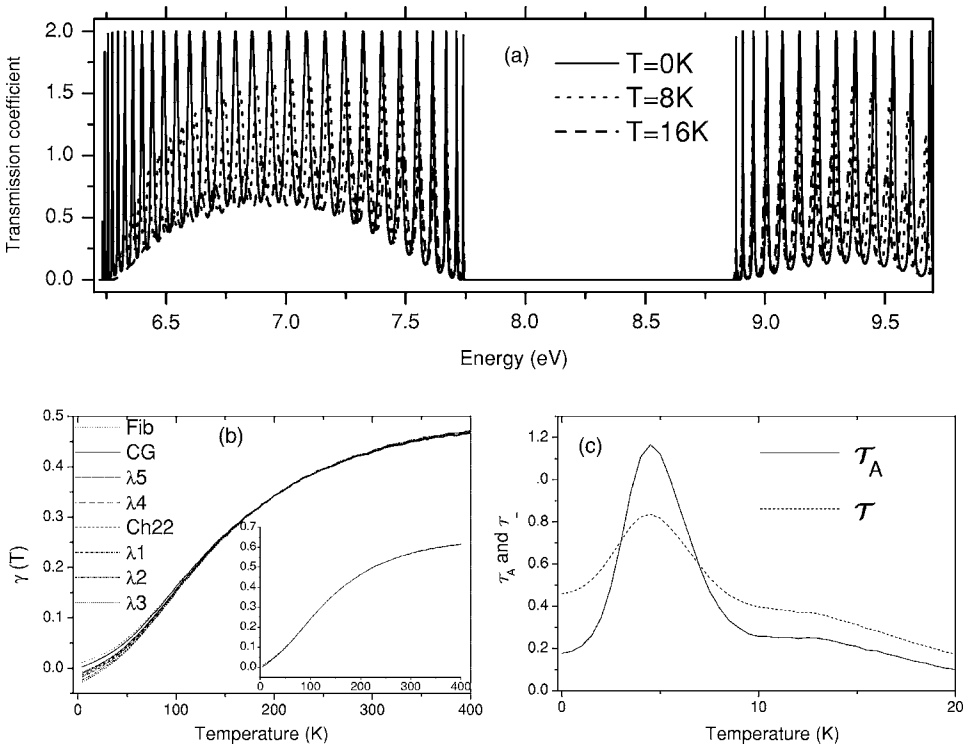

FIG. 4. (a) $\mathcal{T}_A$ of poly(G)-poly(C) sequence vs energy at different temperatures $T=0$, 8, and 16 K. (b) Temperature-dependent Lyapunov exponent $\gamma(T)$ vs temperature for eight kinds of model DNA sequences. An approximate universal behavior is obtained in the sense that all sequences give the same $\gamma(T)$ curve. Inset: Lyapunov exponent for the same sequences but with $t_{DNA}=0.4$ eV. The universal behavior holds although the absolute value of $\gamma(T)$ depends on the hopping parameter. (c) $\mathcal{T}_A$ (solid line) and $\mathcal{T}$ vs temperature at $E=6.378$ eV.

sequence with or without a superconducting electrode: the thermal enhancement of transport for NS systems is significantly larger than that for the normal system. Finally, for a different hopping matrix element $t_{DNA}=0.4$ eV, which is the value obtained from *ab initio* calculation,[18] our general conclusion concerning thermal enhancement of charge transport remains the same. Furthermore, the inset of Fig. 4(b) shows that for $t_{DNA}=0.4$ eV, $\gamma(T)$ for all the model DNA sequences are still a universal function.

In summary, using a simple tight-binding atomic model, we have investigated qualitative features of charge transport through eight different kinds of model DNA sequences with or without a superconducting electrode. At finite temperatures, thermal fluctuations of the twist angle between neighboring base pairs give rise to fluctuations of the hopping matrix element between base pairs with a variable rms value. Due to the change of hopping matrix element, a thermal enhancement of charge transport is observed which we found to be a generic feature of all the model DNA sequences studied. For poly(G)-poly(C) sequences, this enhancement can be observed at $T=20$ K. Larger enhancement is found when a superconducting electrode is present. The Lyapunov exponents are calculated for different model DNA sequences. We found that although the Lyapunov exponents for different model DNA sequences can be different at zero temperature, its temperature-dependent part is approximately a universal function of temperature. In the presence of a superconducting electrode, the Lyapunov exponent doubles the value of the normal system. Since I-V characteristics of various DNA sequences have already been experimentally measured, the thermal enhancement effect should be experimentally testable. A measurement of the Lyapunov exponent as a function of temperature, while an experimental challenge, should also be possible. Finally, another interesting problem would be a theoretical study of the variable-range-hopping model in the presence of a superconducting lead. The technique in Ref. 22 can perhaps provide a starting point along this line.

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