Variable Range Hopping and Electrical Conductivity along the DNA Double Helix

Z. G. Yu and Xueyu Song
Department of Chemistry, Iowa State University, Ames, Iowa 50011
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We present a model to describe electrical conductivity along the DNA double helix. In this model, DNA is considered as a one-dimensional disordered system, and electrons are transported via variable range hopping between localized states. Thermal structural fluctuations in DNA further localize electronic wave functions, giving rise to a temperature-dependent localization length. The model quantitatively explains the temperature dependence of the conductivity observed in the lambda phage DNA (λ-DNA).

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Electron transfer and transport along DNA are important in radiation damage and repair and in biosynthesis [1–4]. Recent experiments have demonstrated long-range charge migration along the DNA double helix, indicating that DNA is a candidate for a one-dimensional (1D) molecular wire [5–7]. However, existing conductivity data of DNA are inconsistent with one another [8–10], which has been attributed to electron-bombardment-induced contaminations [11] and strong contact effects [12]. While accurate determination of absolute values of conductivity is important, characteristic temperature dependences of the conductivity often provide clues to mechanisms of transport. Recently Tran *et al.* used the resonant cavity technique and systematically studied conductivity and its temperature dependence along the DNA double helix [12]. It is found that at high temperatures the conductivity can be described as $\sigma \propto \exp(-E/k_BT)$, with $E = 0.15$ eV for dry lambda phage DNA (λ-DNA) samples and $E = 0.165$ eV for λ-DNA lyophilized in buffer samples, whereas at low temperatures the conductivity in both the dry λ-DNA and the λ-DNA in buffer exhibits a very weak temperature dependence. The crossover occurs at about 200–250 K. While the high temperature behavior suggests that charge transport is due to the temperature driven activation process, the underlying physics of the weak temperature dependence at low temperatures and the mechanism leading to the crossover with decreasing temperature are not yet understood. It has been speculated that at a low temperature regime the ionic conduction rather than the electronic conduction may be the primary contribution to the conductivity [12].

In this Letter, we show that the observed temperature-dependent conductivity in DNA can be consistently modeled, without invoking additional ionic conduction mechanisms, by considering that electrons may use variable range hopping for conduction and that electron localization is enhanced by strong thermal structural fluctuations in DNA.

A DNA double helix with a random base pair sequence can be viewed as a 1D disordered system. In this system, the disorder leads to electronic localization, and electron hoppings between these localized "impurity" states along the chain are responsible for the conductivity. The probability for a hop from an occupied site to a vacant site separated by a distance R is approximately $P \sim \exp[-2\alpha R - W/k_BT]$ [13], where α^{-1} is the localization length and W is the energy difference between two sites. According to Mott's variable range hopping argument [14,15], there is competition between the two terms in the exponential, and an electron may optimize its hopping distance R to achieve the largest hopping rate. Recent charge transfer studies of DNA have shown that two competing mechanisms, unistep superexchange and multistep hopping, contribute to the charge migration [16,17], which is consistent with this variable range hopping picture. If we assume that site energy has a uniform distribution between $-\Delta$ to Δ, the average energy spacing for sites separated by a distance R would be $\Delta a/R$, where a (= 3.4 Å) is the distance between the nearest neighboring bases. We have

$$P \sim \exp\left[-2\alpha R - \frac{\Delta a}{R k_B T}\right]. \tag{1}$$

The most likely hopping distance R_0 is determined by maximizing this expression, $R_0 = \sqrt{\Delta a/2\alpha k_B T}$. Accordingly, the conductivity σ would be

$$\sigma \sim \exp[-\sqrt{8\Delta a\alpha/k_BT}]. \tag{2}$$

Equation (2) characterizes variable range hopping at low temperatures, which has a weaker temperature dependence than an activated behavior. It applies provided that R_0 is larger than the distance between the nearest neighboring bases, a. If R is smaller than a, the conductivity has the usual temperature-dependence characteristic of activated behavior, $\sigma \sim \exp(-\Delta/k_BT)$. The criterion, $R_0 = a$, naturally gives the crossover temperature,

$$k_BT_c = \Delta/2\alpha a. \tag{3}$$

Thus, according to the variable range hopping picture, one would expect a crossover of temperature dependence of σ. Above T_c, electron transport is via the nearest neighbor hopping and is a simple activation process, whereas below T_c, electrons may optimize their paths by using the variable range hopping, resulting in a weaker temperature dependence. The variable range hopping and resultant temperature dependence of conductivity in 1D systems have also

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been analyzed based on the percolation theory [18]. Lee and co-workers [18] found that the resistance ρ $(= \sigma^{-1})$ in a disordered chain with an intermediate length L can be described as $\langle\rho\rangle \sim \exp(T_0/T)^{1/2}[\ln(2\alpha L)]^{1/2}$, where $T_0 = 2\alpha a\Delta$.

Although the above variable range hopping model predicts a crossover and a weaker temperature dependence at low temperatures than at high temperatures, it is not sufficient to quantitatively explain the experimentally observed temperature dependence in DNA. Using the values of Δ and α determined by the slope of high temperature data and the crossover temperature, we find that the temperature dependence given by Eq. (2) is too strong at low temperatures.

DNA is quite different from inorganic materials in that DNA chains are flexible and have strong structural fluctuations, which may crucially affect the transport properties. In fact, molecular geometry fluctuations were found to be responsible for the ubiquitous Poole-Frenkel behavior of field-dependent mobility in conjugated polymers [19]. Experimentally, structural fluctuations in DNA were observed in dynamic Stokes shifts in the fluorescence spectrum [20]. It was also found theoretically that twist angle fluctuation modes in DNA are soft, with typical frequencies lower than 25 cm^{-1} [21]. Bruinsma *et al.* [22] recently proposed a model to explain the observed two time scales of electron transfer in DNA based on the temperature driven fluctuations in the relative rotation of adjacent bases and in the displacement of bases.

We notice that thermal structural fluctuations in DNA, especially soft twist angle fluctuations between neighboring base pairs, will considerably limit electron transport through DNA and make electron wave functions more localized. Moreover, the electronic localization length should be a function of temperature due to the thermal nature of these fluctuations. To address the effect of thermal structural fluctuations on electron localization, we consider a simplified tight-binding model,

$$H = \sum_l [-t_0 \cos\theta_{ll+1}(c_l^\dagger c_{l+1} + \text{H.c.}) + \epsilon_l c_l^\dagger c_l], \quad (4)$$

where $c_l^\dagger(c_l)$ is the creation (annihilation) operator for an electron on site l, the site energy ϵ_l is a random variable (static disorder) that follows a rectangular distribution from $-\Delta$ to Δ, and θ_{ll+1} is a relative twist angle deviated from its equilibrium value between sites l and $l + 1$. In this model, twist angle fluctuations decrease the overlap of electronic wave functions on adjacent sites. We do not explicitly take account of the on-site energy fluctuation, which can be absorbed into the static energy disorder.

The behavior of the electronic localization parameter, α, can be studied by calculating the participation ratio of this 1D lattice model, $\langle L_{\text{loc}}^{-1}\rangle = \sum_{\mu l} |\psi_\mu(l)|^4/N$, where N is the total number of the lattice sites and $\psi_\mu(l)$ is the wave function of the μth eigenstates. For simplicity, we consider each θ_{ll+1} as an independent random variable that follows a Gaussian distribution with average $\langle\theta_{ll+1}\rangle = 0$. The variance is, according to the equipartition law, $\langle\theta_{ll+1}^2\rangle = k_B T/I\Omega^2$, where I is the reduced moment of inertia for the relative rotation of the two adjacent bases and Ω is the oscillator frequency of the mode.

In Fig. 1, we present the participation ratio, $\langle L_{\text{loc}}^{-1}\rangle$, as a function of temperature. The solid line is for a system with both static disorder and thermal twist angle fluctuations, and the dot-dashed line is for a system with only thermal fluctuations. The similar shapes of these two lines suggest that the localization parameter α may be written as $\alpha = \alpha_0 + \alpha_d$, where α_0 is due to static disorder and α_d is due to thermal structural fluctuations. At low temperatures, the fluctuation of θ_{ll+1} is small and the hopping integral is $t_0 - \delta t \simeq t_0(1 - \theta_{ll+1}^2/2)$. By using the Born approximation [23], we have $\alpha_d \sim \langle(\delta t)^2\rangle \sim \langle\theta_{ll+1}^4\rangle \sim T^2$. With increasing temperature, thermal structural fluctuations become stronger and the localization length parameter α becomes larger. However, α cannot increase indefinitely and must saturate at some point (as shown in Fig. 1), because when the localized electronic wave functions become extremely localized, they essentially do not feel any interbase structural fluctuations. Hence we propose, in DNA,

$$\alpha = \alpha_0 + \alpha_1 \tanh(T/T_d)^2, \quad (5)$$

which is central to this paper because it determines the electronic localization length at different temperatures. Equation (5) has the correct behaviors at both low and high temperatures. Furthermore, the calculated participation ratio curve can be well described by this expression, as shown in Fig. 1. If we substitute Eq. (5) into Eq. (2), we expect that including thermal structural fluctuations will lead to a weaker temperature dependence of conductivity in the variable range hopping regime.

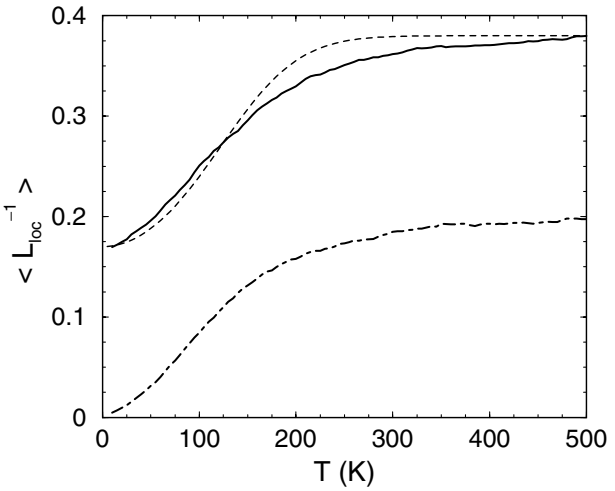

FIG. 1. Participation ratio as a function of temperature. Dot-dashed and solid lines correspond to $\Delta = 0$ and 0.15 eV, respectively. Other parameters are $t_0 = 0.1$ eV, $I\Omega^2/k_B = 250$ K, and $N = 1000$. The dashed curve represents the expression, $0.17 + 0.21\tanh(T/170)^2$.

Parameters α_0 and α_1 in Eq. (5) for DNA can be estimated from existing experimental data and quantum chemistry calculations. We determine α_0 from the localization length expression for 1D systems with only static disorder [24], $\alpha_0 a \simeq 0.1142(\Delta/t_0)^2$. *Ab initio* molecular-orbital calculations show that the transfer integral of two stacked nucleobases is of order 0.1 eV [25]. We choose, conservatively, $t_0 = 0.065$ eV for disordered DNA chains, and $\Delta = 0.15$ eV according to the conductivity data, and obtain $\alpha_0 = 0.18$ Å^{-1}. The largest value of α at room temperature, observed from the distance dependence of electron transfer experiments performed in DNA [16], is 0.8 Å^{-1}, which should be close to the saturation value of α. We choose $\alpha_1 = 0.7$ Å^{-1}, and the saturation value is 0.88 Å^{-1}, which corresponds to localization length 1.1 Å, much less than 3.4 Å, the distance between adjacent bases. Parameter T_d in our model controls how fast α saturates as increasing temperature, which is associated with the characteristic energy of the twist angle fluctuations, $I\Omega^2$, with a typical value of $100\text{–}200k_B$ [22].

To quantitatively study the temperature-dependent conductivity in DNA, we numerically calculate the dc conductivity of DNA chains [26]. In the linear-response regime, it has been shown that this conductivity problem is equivalent to finding an effective resistance of a random impedance network [13,27], in which each pair of sites, i and j, is connected by a resistance Z_{ij} [28],

$$Z_{ij}^{-1} = \frac{e^2}{k_B T} f_i^0(1 - f_j^0) w_{ij}^0 = \frac{e^2}{k_B T} f_j^0(1 - f_i^0) w_{ji}^0 ,$$

where f_i^0 is the equilibrium occupation of site i, $f_i^0 = [1 + e^{(\epsilon_i - \mu)/k_B T}]^{-1}$. w_{ij}^0 is the hopping rate from site i to site j in the equilibrium, which has the Miller-Abrahams form [13], i.e., $w_{ij}^0 = \nu e^{-2\alpha R_{ij}} e^{(\epsilon_i - \epsilon_j)/k_B T}$ if $\epsilon_i < \epsilon_j$ and $\nu e^{-2\alpha R_{ij}}$ if $\epsilon_i > \epsilon_j$. ν is an overall multiplicative factor, which can be determined by fitting experimental data or by first-principles calculations [11]. In the numerical calculations, the chemical potential is fixed, $\mu = 0$ (i.e., half-filled), and α has the form of Eq. (5). The system in the calculation contains 16×16 isolated chains with a length of 128 bases. The electron transport is assumed to occur along these chains. We change the chemical potential and increase the system size, and find that the results virtually do not change.

Figure 2 plots conductivity as a function of inverse temperature. It is shown that our model gives a crossover of the conductivity with decreasing temperature. Above the crossover temperature, the conductivity has an activated behavior, whereas below this temperature, the conductivity depends very weakly on temperature. If electron hoppings are restricted to nearest neighbor hoppings, the temperature dependence would be a simple activated behavior over the entire experimental accessible range of temperature, as described by the dot-dashed line. Thus the variable range hopping is needed to account for the weak temperature dependence at low temperatures. If there exists static disorder only, as depicted by the dashed line (although at low temperatures the temperature dependence is weaker than the activated behavior), it is too strong to explain the observed temperature dependence in DNA. At high temperatures the solid line merges with the dot-dashed line, indicating that electron hopping comes mainly between adjacent sites.

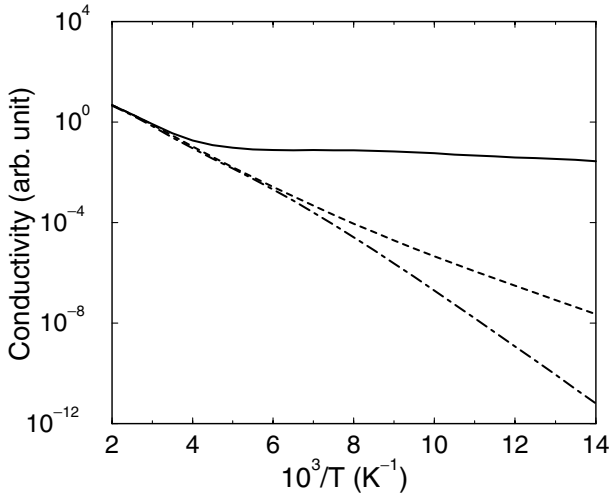

FIG. 2. Logarithm of conductivity σ versus inverse temperature. The solid line is the result of our model with $\alpha_0 = 0.18$ Å^{-1}, $\alpha_1 = 0.7$ Å^{-1}, and $T_d = 200$ K. The dot-dashed line shows the result of a system where electrons can only hop to nearest neighbors. The dashed line shows the result of a system with only static disorder, $\alpha = \alpha_0 = 0.88$ Å^{-1}.

Figure 3 shows the temperature-dependent conductivity with different T_d. T_d is a parameter used to measure the strength of thermal structural fluctuations and controls the saturation rate of α as increasing temperature. From Fig. 3, we see that T_d determines where the crossover of

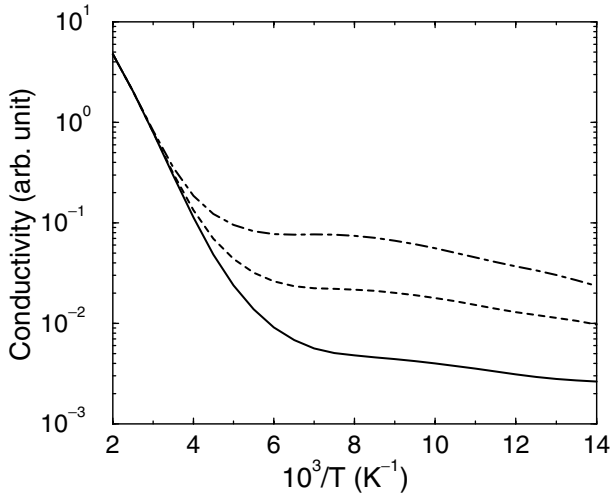

FIG. 3. Logarithm of conductivity σ versus inverse temperature for different T_d. Solid, dashed, and dot-dashed lines correspond to $T_d = 150$, 175, and 200 K, respectively. Other parameters are $\alpha_0 = 0.18$ Å, $\alpha_1 = 0.7$ Å, and $\Delta = 0.15$ eV.

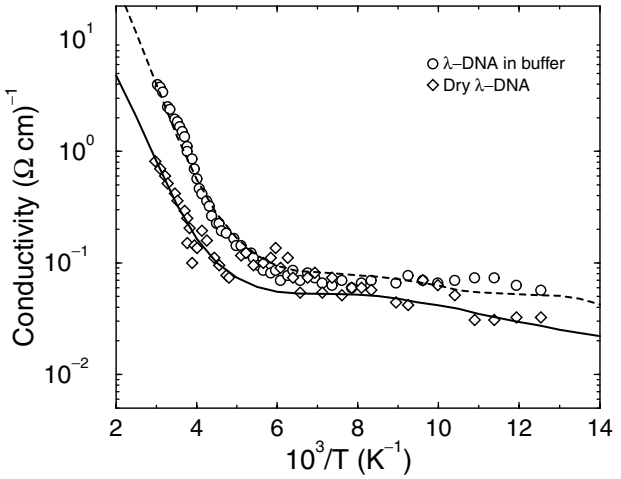

FIG. 4. Logarithm of conductivity σ versus inverse temperature. Circles and diamonds are experimental data measured at 12 GHz for the λ-DNA in buffer and the dry λ-DNA, respectively (Ref. [12]). The dashed line is our theoretical result with $T_d = 175$ K and $\Delta = 0.165$ eV. The solid line is our theoretical result with $T_d = 192$ K and $\Delta = 0.15$ eV.

temperature dependence will occur. For a smaller T_d, the crossover occurs at a lower temperature.

To interpret conductivity measurements for the dry λ-DNA and the λ-DNA in buffer, we fit the conductivity data by adjusting T_d with fixed $\alpha_0 = 0.18$ Å^{-1} and $\alpha_1 = 0.7$ Å^{-1}. We find excellent fits for both the dry λ-DNA and the λ-DNA in buffer, as shown in Fig. 4. The DNA in buffer is in a water-rich environment, which has a higher relative humidity than the dry DNA. The smaller value of T_d in the λ-DNA in buffer ($T_d = 175$ K) than that in the dry λ-DNA ($T_d = 192$ K) is consistent with the fact that, in DNA, twist angle fluctuation modes become softer with increasing relative humidity, as observed in Raman measurements [29].

In summary, we have proposed a model to describe electrical conductivity in DNA, in which DNA is regarded as a 1D disordered system, and electron hopping between localized states is the main mechanism for electrical conductivity in DNA. Strong thermal structural fluctuations in DNA further localize electronic wave functions and result in a temperature-dependent localization length. As decreasing temperature, the conduction mechanism changes from the nearest neighbor hopping to the variable range hopping, giving rise to a crossover from an activated behavior at high temperatures to an extremely weak temperature dependence at low temperatures. Our results quantitatively agree with conductivity measurements of λ-DNA and indicate that variable range hopping may be crucial to the understanding of electron transport in DNA.

[1] M. R. Arkin *et al.,* Science **273**, 475 (1996).
[2] C. J. Murphy *et al.,* Science **262**, 1015 (1993).
[3] D. N. Beretan *et al.,* Science **258**, 1740 (1992).
[4] M. D. Purugganan *et al.,* Science **247**, 6548 (1988).
[5] F. D. Lewis *et al.,* Science **277**, 673 (1997).
[6] D. B. Hall, R. E. Holmlin, and J. K. Barton, Nature (London) **382**, 731 (1996).
[7] P. J. Dondliker, R. E. Holmlin, and J. K. Barton, Science **257**, 1465 (1997).
[8] E. Broun *et al.,* Nature (London) **391**, 775 (1998).
[9] H. W. Fink and C. Schonenberger, Nature (London) **398**, 407 (1999).
[10] D. Porath *et al.,* Nature (London) **403**, 635 (2000).
[11] P. J. de Pablo *et al.,* Phys. Rev. Lett. **85**, 4992 (2000).
[12] P. Tran, B. Alavi, and G. Gruner, Phys. Rev. Lett. **85**, 1564 (2000).
[13] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[14] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Solids* (Oxford University, London, 1971).
[15] In literature, it was argued that the resistance of one-dimensional systems is governed by the hardest hop, and one finds a simple $\ln\sigma \sim 1/T$ activated behavior. However, it has been realized that this result is valid only for sufficiently long chains and long time observation, while for immediate lengths, as in DNA, $\ln\sigma \sim 1/T^{1/2}$ dependence is still valid.
[16] J. Jortner *et al.,* Proc. Natl. Acad. Sci. U.S.A. **95**, 12 759 (1998), and references therein.
[17] M. Ratner, Nature (London) **397**, 480 (1999), and references therein.
[18] P. A. Lee, Phys. Rev. Lett. **53**, 2042 (1984); R. A. Serota, R. K. Kalia, and P. A. Lee, Phys. Rev. B **33**, 8441 (1986).
[19] Z. G. Yu, D. L. Smith, A. Saxena, R. L. Martin, and A. R. Bishop, Phys. Rev. Lett. **84**, 721 (2000).
[20] E. Brauns *et al.,* J. Am. Chem. Soc. **121**, 11 644 (1999).
[21] S. Cocco and R. Monasson, J. Chem. Phys. **112**, 10 017 (2000).
[22] R. Bruinsma, G. Gruner, M. R. D'Orsogna, and J. Rudnick, Phys. Rev. Lett. **85**, 4393 (2000).
[23] N. F. Mott, Adv. Phys. **16**, 49 (1967).
[24] E. N. Economou, *Greens Functions in Quantum Physics* (Springer-Verlag, Berlin, 1983).
[25] H. Sugiyama and I. Saito, J. Am. Chem. Soc. **118**, 7063 (1996).
[26] In this disorder model, the conductivity increases with increasing frequency. At low frequencies, the conductivity for a given frequency exhibits a similar temperature dependence as the dc conductivity [14].
[27] V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971).
[28] M. Pollak and A. Hunt, in *Hopping Transport in Solids,* edited by M. Pollak and B. Shklovskii (North-Holland, Amsterdam, 1991).
[29] H. Urabe, Y. Sugawara, M. Tsukakosji, and T. Kasuya, J. Chem. Phys. **95**, 5519 (1991).