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2009 J. Phys.: Condens. Matter 21 035114

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Correlated small polaron hopping transport in 1D disordered systems at high temperatures: a possible charge transport mechanism in DNA

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Received 29 April 2008, in final form 21 November 2008

Published 15 December 2008

Online at stacks.iop.org/JPhysCM/21/035114

Abstract

Based on the generalized molecular crystal model (GMCM) and theoretical percolation arguments we investigate small polaron hopping transport in 1D disordered systems at high temperatures. Correlation (cr) effects are taken into account. An analytical expression for the temperature dependence of the electrical conductivity, $\ln \sigma^{h,cr} \sim T^{-1/2}$, is obtained. This result reproduces satisfactorily the experimental data reported for λ -DNA and for poly(dA)–poly(dT) DNA, considering DNA as a one-dimensional disordered molecular wire in which small polarons are the charge carriers. $\ln \sigma^{h,cr}$ versus $T^{-1/2}$ plots permit the evaluation of the maximum hopping distance. The results indicate that correlation effects are probably responsible for large hopping distances in DNA samples.

1. Introduction

In recent years one-dimensional (1D) conductors, carbon nanotubes, nanowires and conducting molecules have been considered to be the most promising materials for nanotechnology. As a consequence of this an increasing amount of experimental and theoretical research has been devoted to their electrical properties. Knowledge of the nature of the carriers and the transport mechanism responsible for the measured electrical conductivity, will enable researchers to use these materials for innovative applications and the refinement of many others. When an electron or a hole is injected into a deformable medium it is possible to introduce local distortions of the structure as the latter adjusts to the excess charge and lowers the system's energy [1–3]; in other words a polaronic distortion is expected to be formed. The transport behavior of a polaronic carrier differs significantly from that of a free electron and has to be treated accordingly. On the other hand, the presence of disorder may severely affect the transport mechanism, while external stimuli, such as finite electric fields, play a distinctive role as well. Moreover, high temperatures should be studied for practical reasons. Since all the factors

referred to above could be present in 1D systems of great physical and technological interest [4–9], their inclusion in a systematic theoretical investigation of the electrical behavior of 1D systems is essential.

Recently, Triberis *et al* [10, 11] investigated the phonon-assisted hopping transport of small polarons across a 1D disordered system. The microscopic transport mechanism was treated within the framework of the generalized molecular crystal model [12] and the Kubo formula [13]. The macroscopic behavior of the electrical conductivity, σ , as a function of the temperature was investigated using percolation theory arguments. Correlation effects, in a sequence of successive hops of the carriers, were ignored. The temperature dependence of the electrical conductivity at high temperatures (multi-phonon-assisted hopping) was found to follow a $\ln \sigma^h \sim T^{-2/3}$ law, while at low temperatures (few-phonon-assisted hopping) a $\ln \sigma^h \sim T^{-1/2}$ law was obtained. They applied their theoretical result for the electrical conductivity at high temperatures to recent experimental findings, according to which strong T -dependence was observed in different DNA samples [14, 15]. It was concluded that multi-phonon-assisted small polaron hopping between next nearest neighbors could be the transport mechanism responsible for this behavior.

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From percolation analysis we know that when a carrier hops from one site to another, in the presence of disorder, to ignore the correlations, although it is a plausible first approximation, it is not a realistic one [16]. Triberis [17] and Triberis and Friedman [18] showed the consequences of the inclusion of correlations in small polaron hopping transport in 3D disordered materials.

As far as the T -dependence of the electrical conductivity of DNA is concerned, new experimental data (Inomata *et al* [19]) confirmed the behavior reported by Tran *et al* [14] and Yoo *et al* [15]. Moreover, during the last decade it has become evident that electrons and electron holes migrate through DNA over long distances [20–22].

The above factors motivated the present work, which has a twofold objective: (i) the derivation of an analytical expression for the temperature dependence of the small polaron hopping electrical conductivity of 1D disordered systems, including correlations and (ii) applying our theoretical approach to DNA, the investigation of whether correlation effects could affect the charge transport process across DNA and justify the possibility of long-range charge migration.

2. Theory

2.1. The model

We consider a 1D deformable ‘wire’ consisting of ‘molecular lattice sites’ across which small polarons are transported in the presence of disorder. We assume that the disorder imposed upon a carrier residing on a ‘molecular lattice site’ is energetic. Structural disorder, coming, for example, from a random sequence across the ‘wire’ of different ‘molecular lattice sites’ is not taken into account. By $\epsilon_i(0)$, and $\epsilon_j(0)$ we denote the energies of an electron on site at vector positions \mathbf{r}_i and \mathbf{r}_j , respectively, if the ‘molecular lattice sites’ are constrained not to be displaced in response to the presence of the electron. Due to the disorder these local electronic energies, $\epsilon_i(0)$, and $\epsilon_j(0)$ are not equal. The energetic non-equivalence of the two sites will affect the small polaron’s binding energy, $E_b(i)$, in the sense that, the lower the local electronic energy the more localized the electronic wavefunction will tend to be and consequently the larger will be its binding energy. Assuming that the stiffness of the ‘molecular lattice’ is unaltered, the difference in binding energy means a difference in the electron-lattice interaction parameters A_i and A_j i.e. $E_i(x_i) = \epsilon_i(0) - A_i x_i$ and $E_j(x_j) = \epsilon_j(0) - A_j x_j$ with $A_i \neq A_j$. Here, $E_i(x_i)$ is the electronic energy of the system of the electron and the isolated molecule with configurational coordinate x_i , which represents the deviation of the atoms of the molecule at position \mathbf{r}_i from their equilibrium configuration i.e. the local vibrational displacement coordinate.

For the GMCM the free-field basic equation of motion reads:

$$i\hbar \frac{\partial}{\partial t} [\alpha(\mathbf{r}_i, \dots, q_{\mathbf{k}} \dots; t)] = \sum_{\mathbf{k}} \left[\left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_{\mathbf{k}}^2} + \frac{1}{2} M \omega_{\mathbf{k}}^2 q_{\mathbf{k}}^2 \right) - \left(\frac{2}{N} \right)^{1/2} A_i q_{\mathbf{k}} \sin \left(\mathbf{k} \cdot \mathbf{r}_i + \frac{1}{4} \pi \right) + \epsilon_i(0) \right] \times \alpha(\mathbf{r}_i, \dots, q_{\mathbf{k}} \dots; t) - J \sum_{\mathbf{h}} \alpha_{\mathbf{r}_i + \mathbf{h}}. \quad (1)$$

In this equation, the $\alpha(\mathbf{r}_i, \dots, q_{\mathbf{k}} \dots; t)$ are the amplitudes of the total wavefunction of the system in a tight-binding expansion of the form

$$\Psi(\mathbf{r}, \dots, x_i \dots; t) = \sum_i \alpha(\mathbf{r}_i, \dots, q_{\mathbf{k}} \dots; t) \Phi(\mathbf{r} - \mathbf{r}_i, x_i) \quad (2)$$

in which the Φ are the set of local electronic wavefunctions centred at the various lattice sites \mathbf{r}_i , \mathbf{r} is the electronic coordinate and \mathbf{h} indexes the nearest neighbours ($\mathbf{r}_i + \mathbf{h}$), of an arbitrary site, \mathbf{r}_i ; $(-)J$ is the standard electronic overlap integral of the tight-binding theory assumed to be a constant for all pairs of nearest-neighbour sites.

The matrix elements of the Hamiltonian of the system are

$$\langle m|H|n \rangle = \langle m|H_0 + V|n \rangle = E_{i, \{n_{\mathbf{k}}\}} \delta_{ij} \delta_{\{n_{\mathbf{k}}\}, \{n'_{\mathbf{k}}\}} + \langle m|V|n \rangle,$$

where $|n \rangle = |i, \{n_{\mathbf{k}}\} \rangle$ are the eigenstates of H , and H_0 is the zeroth-order (i.e. for electronic overlap integral of the tight-binding theory $J = 0$) Hamiltonian with corresponding eigenvalues

$$E_{i, \{n_{\mathbf{k}}\}} = \epsilon_i(0) - E_b(i) + \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}} \left(n_{\mathbf{k}} + \frac{1}{2} \right). \quad (3)$$

Here, $\{n_{\mathbf{k}}\}$ represents the totality of the vibrational quantum numbers ($\dots, n_{\mathbf{k}}, \dots$) for the occupation of the site with position vector \mathbf{r}_i , and

$$E_b(i) = \frac{1}{N} \sum_{\mathbf{k}} (A_i^2 / 2M \omega_{\mathbf{k}}^2), \quad (4)$$

is the small polaron binding energy. The relation between $\omega_{\mathbf{k}}$ and its associated wavevector \mathbf{k} , i.e. the dispersion relation, is given by:

$$\omega_{\mathbf{k}}^2 = \omega_0^2 + \omega_1^2 \sum_{\mathbf{h}} \cos(\mathbf{k} \cdot \mathbf{h}), \quad (5)$$

where $|\mathbf{k}| = 2\pi p/N$, the integer p lying in the range $-(N-1)/2 \leq p \leq (N-1)/2$, N being the number of lattice sites.

The $\langle m|V|n \rangle$ term for the GMCM is the overlap part of the Hamiltonian with matrix elements given by

$$\begin{aligned} \langle m|V|n \rangle &= \langle \mathbf{r}_j, \{n'_{\mathbf{k}}\} | V | \mathbf{r}_i, \{n_{\mathbf{k}}\} \rangle \\ &= -J \sum_{\mathbf{h}} \delta_{\mathbf{r}_i, \mathbf{r}_i + \mathbf{h}} \prod_{\mathbf{k}} \left[(1 - (1/N)) \left(n_{\mathbf{k}} + \frac{1}{2} \right) \frac{1}{2M \omega_{\mathbf{k}} (\hbar \omega_{\mathbf{k}})} \right. \\ &\quad \times \{ A_{\mathbf{r}_i + \mathbf{h}}^2 [1 - \lambda \sin(2\mathbf{k} \cdot (\mathbf{r}_i \pm \mathbf{h}))] \\ &\quad + A_{\mathbf{r}_i}^2 [1 - \lambda \sin(2\mathbf{k} \cdot \mathbf{r}_i)] \\ &\quad \left. - 2A_{\mathbf{r}_i} A_{\mathbf{r}_i + \mathbf{h}} [\cos(\mathbf{k} \cdot \mathbf{r}_i) - \lambda \sin(2\mathbf{k} \cdot (\mathbf{r}_i + \frac{1}{2}\mathbf{h}))] \right] \delta_{n'_{\mathbf{k}}, n_{\mathbf{k}}} \\ &\quad \pm \left(\frac{4}{N} \right)^{1/2} \left(\frac{n_{\mathbf{k}} + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \frac{1}{2^{1/2} M^{1/2} \omega_{\mathbf{k}} (\hbar \omega_{\mathbf{k}})^{1/2}} \\ &\quad \times \{ A_{\mathbf{r}_i + \mathbf{h}} \sin[\mathbf{k} \cdot (\mathbf{r}_i + \mathbf{h}) + \frac{1}{4}\pi] \\ &\quad \left. - A_{\mathbf{r}_i} \sin[\mathbf{k} \cdot \mathbf{r}_i + \frac{1}{4}\pi] \right\} \delta_{n'_{\mathbf{k}}, n_{\mathbf{k} \pm 1}}. \end{aligned} \quad (6)$$

Here $\lambda = \mp 1$ according to whether $\mathbf{k} \cdot \mathbf{h}$ is positive or negative, respectively, and $\mathbf{r}_j = \mathbf{r}_i + \mathbf{h}$.

Equations (3) and (4) show the essential features of the GMCM which are:

- (1) site-dependent local electronic energy $\epsilon_i(0)$.
- (2) Site-dependent electron-lattice interaction parameter, A_i , and concomitant binding energy, $E_b(i)$.

The knowledge of $\langle m|V|n \rangle$, permits the evaluation of the ‘microscopic’ small polaron velocity operator [23, 24],

$$u_{ij} = \langle m|u|n \rangle = \left(\frac{i}{\hbar} \right) \langle m|V|n \rangle (\mathbf{r}_j - \mathbf{r}_i), \quad (7)$$

the charge current density operator,

$$j_{ij} = n_c q u_{ij}, \quad (8)$$

where n_c is the charge carrier concentration, and q is the carrier’s charge, and thus the ‘microscopic’ electrical conductivity [13],

$$\sigma_{ij} = \int_0^\infty dt \int_0^\beta d\rho \langle j(-i\hbar\rho)j(t) \rangle, \quad (9)$$

where $\beta = 1/k_B T$ and k_B is the Boltzmann’s constant. Further calculations allow the knowledge of the mobility, μ_{ij} , the diffusion constant, given by $D_{ij} = \mu_{ij}/e\beta$, and consequently the ‘microscopic’ jump rate which reads:

$$L_{ij} = \frac{D_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|^2}. \quad (10)$$

Assuming that the dependence on the spatial separation R_{ij} of the two sites is $\exp(-2\alpha R_{ij})$ [25], α^{-1} being the spatial extent of the electronic wavefunction localized at a single site, the ‘microscopic’ intrinsic transition rate, γ_{ij} , for a small polaron hopping from a site i to an empty site j is given by

$$\gamma_{ij} = \exp(-2\alpha R_{ij}) L_{ij}. \quad (11)$$

Knowing the intrinsic transition rate, we obtain the average equilibrium transition probability [12], W_{ij}^0 :

$$W_{ij}^0 = (W_{ij}^0 W_{ji}^0)^{1/2} = [n_i^0 (1-n_i^0)]^{1/2} [n_j^0 (1-n_j^0)]^{1/2} (\gamma_{ij} \gamma_{ji})^{1/2}, \quad (12)$$

where n_i^0 is the equilibrium occupation probability of the i th site.

2.2. Percolation treatment

According to percolation theory [25] the study of the motion of an electron in a disordered system between localized states, which are randomly distributed in energy and position, is equivalent to the study of the possibility of the passage of electric current through a network of impedances, Z_{ij} , which connect the different lattice sites, i and j , given by

$$Z_{ij} = [(q^2/k_B T)(W_{ij}^0)]^{-1}. \quad (13)$$

Here q is the carrier’s charge.

At high temperatures the average equilibrium transition probability W_{ij}^0 is given by [10]

$$W_{ij}^{0h} = \gamma_0^h \exp(-2\alpha R_{ij}) \exp[-(|E_i| + |E_j| + 2\epsilon_2)/2k_B T]. \quad (14)$$

Here, $\gamma_0^h = (J^2/\hbar)(\pi/4\epsilon_2 k_B T)^{1/2}$, $\epsilon_2 = [E_b(i) + E_b(j)]/4$ and $E_i = \epsilon_i(0) - E_b(i)$ is the electronic energy when the electron resides on site i . Assuming, as shown in [12], that the electronic energy is mainly polaronic, i.e. $|E_i| \simeq E_b(i)$, $|E_j| \simeq E_b(j)$, hereafter we shall refer to the binding energy as the site energy, and we shall use the symbol E_i instead of $E_b(i)$ for convenience.

Thus, the impedances Z_{ij} are given by

$$Z_{ij}^h = Z_0^h \exp(\xi_{ij}^h), \quad (15)$$

where

$$\xi_{ij}^h = 2\alpha R_{ij} + (E_i + E_j)/k_B T, \quad (16)$$

$Z_0^h = k_B T/q^2 \gamma_0^h$ and $k_B' = \frac{4}{3} k_B$.

Because of the exponential dependence of Z_{ij} on R_{ij} , E_i and E_j , the individual impedances change by many orders of magnitude. Therefore, the overall electrical conductivity $\sigma^h = (Z^h)^{-1}$ of the connected network of impedances will be determined by a critical percolation impedance Z_c^h , defined as the largest value of the impedance such that the subset of the impedances with $Z_{ij}^h < Z_c^h$ still contains a connected network which spans the entire system.

The random network can be considered as composed of three parts:

- (i) A set of isolated ‘regions’ of low impedances, each region consisting of a group of sites linked together by impedances with $Z_{ij}^h \ll Z_c^h$.
- (ii) A relatively small number of impedances with Z_{ij}^h of order Z_c^h , which connect together a subset of the low impedance clusters to form an infinite network which spans the system. The set of impedances in categories (i) and (ii) form the so-called ‘critical subnetwork’.
- (iii) The remaining impedances with $Z_{ij}^h \gg Z_c^h$.

It is clear that the impedances of order Z_c^h determine the impedance of the network. The impedances in category (i) could all be set equal to zero without greatly affecting the total impedance—the impedance of the system would still be finite because the current has to pass through impedances of order Z_c^h to get from one end of the system to the other. On the other hand the impedances with $Z_{ij}^h \gg Z_c^h$ make a negligible contribution to the total impedance because they are effectively shorted out by the critical subnetwork of impedances with $Z_{ij}^h \leq Z_c^h$.

The inverse quantity $(Z_c^h)^{-1}$ characterizes the macroscopically observed conductivity of the material.

Due to equations (15) and (16), the condition for percolation reads

$$\xi_{ij}^h \leq \xi_c^h \quad (17)$$

or equivalently

$$\frac{R_{ij}}{r_m^h} + \frac{E_i}{E_m^h} + \frac{E_j}{E_m^h} \leq 1, \quad (18)$$

where $r_m^h = \xi_c^h \alpha^{-1}/2$ is the maximum hopping distance and $E_m^h = k_B T \xi_c^h$ is the maximum site energy.

The conductivity of the specimen is expressed as

$$\sigma^h = \sigma_0^h \exp(-\xi_c^h), \quad (19)$$

where $\sigma_0^h = (Z_0^h)^{-1}$.

From percolation analysis we know that when the site energies are not the same, the energy of the site affects the incoming as well as the outgoing impedances, and this correlates the neighboring Z_s . Thus, lack of correlation between successive impedances in a sequence of successive hops, although it is a plausible first approximation, is not realistic. Consequently, we have to take into account the correlations between impedances coming from the common site.

This new condition imposed on the transport process introduces a different physical mechanism for the transport of the carriers along the chain, and it is expected, as in the case of three-dimensional disordered materials [12, 26] to affect the expression of the temperature dependence of the conductivity that is finally obtained, i.e. a different exponential T -dependence from the $\sigma \sim \exp T^{-2/3}$ [10, 11].

The percolation analysis, previously reported ignoring correlations [10, 11], was referred to $P(Z_c)$ alone as the relevant average number of impedances of magnitude Z_c or less connected to a given site. Including correlations, for a random distribution of sites, we have to evaluate the average number of sites accessible by a bond from a given site of energy E_i , i.e. $P(Z_c^{\text{cr}}|E_i)$, for all possible configurations of sites which satisfy the percolation condition, and then average it with respect to E_i .

$P(Z_c^{\text{cr}}|E_i)$ is given by Pollak [16] as

$$P(Z_c^{\text{cr}}|E_i) = \int_{Z=0}^{Z_c^{\text{cr}}} p(E_j|E_i) p(R_{ij}) dR_{ij} dE_j. \quad (20)$$

Here, $p()$ stands for conditional distribution. In other words $p(Z_c^{\text{cr}}|E_i)$ is the average number of impedances, Z_c^{cr} or less, connected to a site of energy E_i .

For a random distribution of sites, in one dimension, $p(R_{ij}) = N_s$, N_s being the concentration of sites. The distribution $p(E_j|E_i)$ is obtained from the definition of E_j from the percolation condition for all possible configurations of pairs. Then, $p(Z_c^{\text{cr}}|E_i)$ is given by

$$P(Z_c^{\text{cr}}|E_i) = \sum_m \int \int \left(\frac{N(E_j)}{N_s} \right) N_s dR_{ij} dE_j \quad (21)$$

where m extends over all possible configurations of sites and the limits of integrations, for the temperature range of interest, can be specified from the corresponding percolation condition. $N(E_j)$ is the density of states for the j site. For simplicity we assume that we have a band of localized states above the Fermi level. Then the possible configurations of sites are (I) $E_m^h > E_i > E_j$ and (II) $E_m^h > E_j > E_i > 0$, where $E_F \equiv 0$. The integration of the right-hand side of equation (21) extends over surfaces of constant Z in the E_i, E_j and R_{ij} space. Specifically the integration extends over surfaces defined by

$$\frac{R_{ij}}{r_m^{h,\text{cr}}} + \frac{E_i}{E_m^h} + \frac{E_j}{E_m^h} = 1. \quad (22)$$

Thus,

$$P(Z_c^{\text{cr}}|E_i) = \int_0^{E'} \left(\frac{N(E_j)}{N_s} \right) dE_j \left(\int_0^{R'} N_s dR' \right) + \int_E^{E'} \left(\frac{N(E_j)}{N_s} \right) dE_j \left(\int_0^{R'} N_s dR' \right) \quad (23)$$

where each term of the right-hand side of equation (23) corresponds to the particular configuration of sites. Here,

$$R' \equiv (r_m^{h,\text{cr}}/E_m^h)(E_m^h - E_i - E_j), \quad E' \equiv E_m^h - E_i. \quad (24)$$

Assuming $N(E_i) = N(E_j) = N_0 = \text{const}$ over the energy range of interest, and taking the disordered energy as mainly polaronic [12], from equation (23) we obtain

$$P(Z_c^{\text{cr}}|E_i) = \frac{N_0}{2} (r_m^{h,\text{cr}}/E_m^h) [(E_m^h - E_i)^2 + (E_m^h - 2E_i)^2]. \quad (25)$$

Here we have to notice that the particular choice of the form of the density of states (DOS) affects our results. To our knowledge, an analytical expression showing the energy dependence of the DOS for DNA has not been presented in the literature yet, although for certain configurations a number of calculations have been presented [27–29]. In our study we have taken the DOS to be constant over the energy E_m , a usual approximation used in studies of amorphous three-dimensional materials [25, 12]. Earlier studies on disordered systems have been reported on the effect of the model DOS on the behavior of the DC conductivity in the case of small polaron hopping [16, 30, 31].

In order to average $P(Z_c^{\text{cr}}|E_i)$ with respect to E_i we have to consider the probability that states with energy E_i are connected to the critical path. The probability can be shown to be proportional to $P(Z_c^{\text{cr}}|E_i)N(E_i)$ [16]. Thus we obtain the percolation condition

$$\bar{P}(Z_c^{\text{cr}}) = \frac{\int_0^{E_m^h} P(Z_c^{\text{cr}}|E_i)N(E_i) dE_i}{\int_0^{E_m^h} P(Z_c^{\text{cr}}|E_i)N(E_i) dE_i} = \theta \quad (26)$$

where for θ we use the value $\theta \simeq 2$ [32]. Performing the integrations in equation (26) we obtain

$$\bar{P}(Z_c^{\text{cr}}) = \frac{N_0}{2} (r_m^{h,\text{cr}}/E_m^h) (E_m^h)^2 \simeq 2 \quad (27)$$

from which

$$\xi_c^{h,\text{cr}} = (T_0^{h,\text{cr}}/T)^{1/2}. \quad (28)$$

Here, $T_0^{h,\text{cr}} = 6/N_0 k_B \alpha^{-1}$. Thus, the conductivity of the high temperature multi-phonon-assisted small polaron hopping one-dimensional regime, including correlations, is given by

$$\sigma^{h,\text{cr}} = \sigma_0^{h,\text{cr}} \exp \left[- \left(\frac{T_0^{h,\text{cr}}}{T} \right)^{1/2} \right]. \quad (29)$$

For a given temperature, equation (29) is expressed as:

$$\sigma^{h,\text{cr}} = \sigma_0^{h,\text{cr}} \exp(-2r_m^{h,\text{cr}}/\alpha^{-1}), \quad (30)$$

where

$$r_m^{h,cr} = \frac{(T_0^{h,cr})^{1/2} \alpha^{-1}}{2} T^{-1/2} \quad (31)$$

i.e. the maximum hopping distance follows a $T^{-1/2}$ law. Equation (29) allows the evaluation of $T_0^{h,cr}$ from the slope of the fits of the experimental data reported for DNA samples, plotted as $\ln \sigma^h$ -versus- $T^{-1/2}$. Knowledge of $T_0^{h,cr}$ using equation (31) permits the evaluation of the maximum small polaron hopping distance at the temperature of interest.

Here we note that, for 3D disordered systems and uncorrelated hopping transport, Triberis and Friedman [12], based on percolation arguments, reported that a $T^{-\epsilon/(\epsilon+r)}$ law governs the T -dependence of the small polaron hopping conductivity. Here, ϵ is the dimensions (number) of the energy and r the spatial dimensions involved in the percolation condition. At high temperatures, where $\epsilon = 2$ and $r = 3$, a $T^{-2/5}$ law was obtained, while at low temperatures, where $\epsilon = 1$ and $r = 3$, the corresponding law is $T^{-1/4}$. However, for the case of correlated hopping, at low as well as at high temperatures, a $T^{-1/4}$ law was obtained for 3D materials [17, 18]. For the case of longitudinal conduction at low temperatures in thin films ($\epsilon = 1$ and $r = 2$) a $T^{-1/3}$ law was obtained [16]. The above have been widely applied to a variety of amorphous materials. A brief review is presented in [33].

For the 1D case, the expression of the T -dependence of the small polaron hopping conductivity derived at high temperatures and uncorrelated hopping, i.e. the $T^{-2/3}$ law [10, 11], as well as the $T^{-1/2}$ law [10, 11] for the low- T case, are consistent with the above predictions. Taking into account correlations, the $T^{-1/2}$ law obtained in our present treatment is, as expected, also consistent with the corresponding 3D case.

3. Small polaron correlated hopping transport: a possible transport mechanism in DNA

The general expression for the electrical conductivity produced in section 2 is applicable to any 1D deformable disordered system in which small polarons are the charge carriers responsible for the observed conductivity. DNA is a potential candidate, for the following reasons:

(i) *Formation of small polarons.* Many theoretical studies support the idea of the formation of polarons in DNA [6–8] and polaron hopping transport as the mechanism responsible for the observed conductivity [34, 9, 35, 36]. Alexandre *et al* [37] reported *ab initio* calculations for poly(dC)–poly(dG) DNA, with up to four C–G pairs. They found a strong hole–lattice coupling and clear evidence for formation of small polarons and estimated the activation energy for polaron hopping and the polaron binding energies.

As Conwell points out [9] two kinds of polarons can be formed in DNA. The so-called ‘distortion’ polaron, where the distortion of the ‘molecular’ lattice site results in the self-trapping of the carrier and the formation of the small polaron, and the ‘solvated’ polaron [38, 39], which differs from ‘distortion’ polaron because its formation is due to polarization by the excess charge of the medium surrounding the DNA, water and ions.

In the application of our theory the polarons considered are of the first kind. For this reason we use experimental data reported for dry samples.

(ii) *Presence of disorder.* Tran *et al* [14] emphasized that the models proposed for the interpretation of the electrical conductivity data did not take into account the disorder associated with the random base sequences, and also the random potentials along the DNA double helix arising from the randomly positioned counterions. The influence of counterion-induced disorder in DNA conduction has been recently investigated by Adessi and Anantram [40]. In DNA disorder is imposed upon the carrier from the nucleobases system, the backbone system and the environment.

According to the GMCM, all the contributions to disorder, excluding the disorder induced by the formation of the polaron, are embodied in the local electronic energy, $\epsilon_i(0)$. As we discussed, in the model the site dependent local electronic energy results in site dependent binding (polaronic) energies. We assume, as shown in [12], that the electronic energy is mainly polaronic, i.e. the induced disorder due to the randomness of binding energies is predominant. The implications of this assumption will be discussed in section 4.

Here we have to note that the generalized molecular crystal model upon which the study of the small polaron hopping conductivity is based was first introduced for the interpretation of the behavior of the conductivity of amorphous materials. There, the concept of ‘disorder’ due to randomly distributed lattice sites or the possible existence of voids etc can be much more easily understood than in the DNA-case.

In DNA we have the basic DNA double helix sequence formed by the specific base pairs (‘lattice sites’) sequence, correlated with the position of phosphates that essentially determine the symmetry of the DNA structure and other environmental factors, e.g. the presence of counterions. As it has been pointed out [41], the sequence dependent DNA conformation (the actual twisting, stretching and bending of the double helix) may not only reflect the tendency of the base pairs to stack at distances and angles dependent on their identity but may also depend on interactions with other molecules or other environmental factors, e.g. cations in the crystallization buffer. Analysis of how the DNA conformation depends on the nucleotide sequence is complicated by variations in the stacking geometry of the base pairs at each specific step with the surrounding sequence. All the above introduce an accumulating disorder under which the small polaron follows a directional walk of successive hops of random length (the random resistance network in our percolation approach).

According to [42, 43] a ‘long-range order model’ for the description of the DNA chain does not seem to be physically appropriate for DNA, while a much more realistic model could be a ‘short-range order model’ in which the mismatches in positions of charges accumulate along the lattice. This model incorporates the sequence specificity of the DNA structure.

(iii) Although the wavefunction of the carrier may be more concentrated at one member of the pair, depending on the ionization energy, e.g. G in G–C, there is good evidence for wavefunction overlap in the pair; it is well documented that

a carrier residing in the pair easily makes a transition to the other [44, 45]. However, if a carrier is located on one strand, it is likely that the transfer will take place on this strand. The actual case depends on the kinds of bases that are included in the sequence. Calculations for the two cases do not lead to very different properties for the polaron [9]. Under these conditions, we believe that our model could be applied whether the transport occurs along one strand or a double helix.

The electrical properties of the DNA and the physical mechanisms behind them are still an open problem and the controversial experimental findings are indicative of this fact. Some reports show insulating characteristics, others semiconducting and even metallic properties have been attributed to DNA. The diversity of the research results on the electrical properties of DNA molecules can be attributed to a variety of factors [46]. Some concerns for the contradicting experimental results are:

Different DNA samples. Variations in length and states of DNA affect the measured conductivity. As expected, the longer the DNA molecules are, the less conductive they appear, while the conductivity of DNA molecules in wet states is greater than in dry states. Also, molecules with different base sequence are characterized by different bends and distortions along the DNA double helix. The variation of the DNA sequence amongst the DNA samples directly affects the charge carriers and hence the conductivity measurements. Usually, positive charge is more stable on a G–C base pair than on an A–T pair due to the different number of hydrogen bonds that connect the complementary bases; there are triple hydrogen bonds in the G–C pairs, but double hydrogen bonds in the A–T pairs. The energy difference between these two pairs is substantially larger than the thermal energy of the charge carrier. So, A–T base pairs may act as a barrier to the transfer. However, the carrier can tunnel in a coherent fashion from the first G–C site to the second, and can then either hop back to the first G–C pair or move on to the next one. Eventually, the number and sequence of base pairs lead to various experimental results.

Variations of sample treatment in different buffer solutions and different experimental environments. Solutions may help the electron transport or the solution itself may be conductive. For instance, DNA in a buffer is in a water-rich environment and different water contents lead to different DNA modifications and different amounts of disorder along the double helix. Consequently, this may lead to a more/less effective charge localization, and thus smaller/greater conductivity. Temperature and humidity may also affect the electrical properties of DNA. It has been shown that DNA electrical conductivity is strongly dependent around room temperature with a crossover to a weakly temperature dependent conductivity at low temperatures [14, 19, 15, 47]. The electrical properties of DNA are also humidity dependent [48]. In aqueous solutions, the phosphates of the double helix face towards water and this stabilizes the double strand. Humidity changes also affect the electrical conductivity of DNA. As reported [48], the resistance of poly(dG)–poly(dC) decreases dramatically with increasing relative humidity. In particular, resistance decreases from $10^9 \Omega$ at 30% relative humidity to about $10^6 \Omega$ at 90% relative

humidity. Therefore, ionic conduction was found to dominate under atmospheric conditions.

Quality of electrical contacts in different experiments. The contact resistance between the electrode and DNA affects the total conductivity of the DNA–electrode system [48]. Measurements of the electrical properties of DNA can be either contactless microwave measurements or direct contact measurements. In the direct contact measurements it is very difficult to ensure that the DNA molecule is in direct contact with the metal electrodes (usually Au). However, even if contact is attained, the weak physical adhesion between DNA and Au may produce an insulating contact and possibly account for the wide variation in reported resistivity [49]. A better approach could achieve direct chemical bonding between the open ends of DNA and Au [50].

Despite the various factors referred to above which affect the measured conductivity, recent experimental reports [14, 19, 15, 47] have revealed an impressive common characteristic in the behavior of the measured conductivity of different DNA samples: the same strong temperature dependence of the conductivity at high temperatures. To our knowledge a consistent interpretation of this behavior has not been presented in the literature. We believe that our theoretical analysis could contribute to this.

Tran *et al* [14] measured the conductivity and its temperature dependence along the lambda phage DNA (λ -DNA) double helix. They used a configuration which does not require contacts to be attached to the specimen under study and measured the temperature dependence of the conductivity associated with the DNA double helix at high frequencies. The conductivity was evaluated from the loss of highly sensitive resonant cavities operating at 12 and 100 GHz. The technique and the analysis which leads to the evaluation of the conductivity from the measured losses are well established [51]. DNA specimens used in their study were lambda phage DNA (λ -DNA) extracted from *Escherichia coli*. In their study DNA strands were treated as thin wires of diameter 2 nm. The ‘DNA in buffer’ samples were DNA lyophilized in buffer and the ‘dry DNA’ samples were purified DNA. The DNA in buffer samples were lyophilized from a solution in 1 mM Tris-HCl, pH 7.5, 1 mM NaCl, 1 mM EDTA and 330 g ml⁻¹ DNA. Lyophilization led to 0.5 mg of DNA in a total weight of 4.9 mg. Approximately 80% of the DNA was of full length and approximately 20% was shared, shorter segments. Purification in the dry DNA samples was performed according to standard processes. Approximately 85% of the total weight was associated with DNA, and the remaining 15% was due to water and residual counterions.

Tran *et al*'s [14] low temperature data were attributed to ionic conduction due to counterions. It was also reported that such ionic conduction cannot account for the strong temperature dependence and the large conductivity they observed at high temperatures—this was attributed to carrier excitations across single particle gaps or temperature driven hopping transport processes. Alternatively, they noticed that the observed behavior would occur when phonon-assisted polaron hopping is the actual transport mechanism.

We consider the experimental data of Tran *et al* [14] (I) for dry λ -DNA at 12 GHz. A pronounced strong temperature

dependent conductivity was observed from 227 to 342 K, i.e. in a 115 K-wide, temperature region. The corresponding values of the conductivity varied from $0.28 \Omega^{-1} \text{ cm}^{-1}$ up to $4.29 \Omega^{-1} \text{ cm}^{-1}$, respectively.

More recently Inomata *et al* [19] measured the electrical current–voltage characteristics of λ -DNA in a vacuum using fine electrodes. The temperature dependence of the conductivity of λ -DNA was indicative of thermally activated hopping behavior and was explained by the Arrhenius equation. In their experiments each λ -DNA molecule had 48 502 base pairs corresponding to a length of $16.5 \mu\text{m}$. They diluted the λ -DNA solution with a TE buffer solution (10 mM Tris-HCl and 1 mM EDTA in distilled water, pH 8.0) of the same composition to a concentration of $35 \mu\text{g ml}^{-1}$. A droplet of dilute DNA solution was deposited onto the substrate followed by the removal of the solvent by suction using a syringe. λ -DNA molecules were extended on the substrate as the air–water interface receded. The I – V measurements of these samples were performed in a vacuum.

The experimental data of Inomata *et al* [19] (II) for λ -DNA showed pronounced strong temperature dependent conductance from 118 to 265 K, i.e. in a 147 K-wide temperature region. The corresponding values of the conductance varied from $0.86 \times 10^{-11} \Omega^{-1}$ up to $1.46 \times 10^{-7} \Omega^{-1}$, respectively. Their experimental data showed similar temperature dependence to that reported by Tran *et al* [14].

Yoo *et al* [15] reported measurements of electrical transport through poly(dA)–poly(dT) and poly(dG)–poly(dC) DNA molecules containing identical pairs. Their measured I – V characteristics at various temperatures were interpreted using a small polaron hopping model [52]. For the poly(dA)–poly(dT) regime they estimated the hopping distance to be about 1.68 nm (5 base pairs) at 300 K, while for poly(dG)–poly(dC) they found it to be 2.5 nm (7 base pairs), independently of the temperature for $T > 50$ K. Their effort to interpret the temperature dependence of the conductivity observed by Tran *et al* [14], using the same polaron hopping model over the whole temperature range, was not very convincing and therefore they did not exclude other possible mechanisms.

The specimens used in their experiments were poly(dG)–poly(dC) and poly(dA)–poly(dT). The average length of poly(dG)–poly(dC) was about 1.7–2.9 μm (5000–8600 base pairs) and that of poly(dA)–poly(dT) was about 500–1500 nm. Electrical contacts between DNA molecules and metal electrodes were made using the electrostatic trapping method. A drop of DNA aqueous solution was positioned on top of the gap between the electrodes, and after trapping, the molecule between the electrodes the sample was dried.

Considering the experimental data of Yoo *et al* [15] (III) for poly(dA)–poly(dT) DNA, a strongly temperature dependent conductivity was also observed from 178 to 306 K, i.e. in a 128 K-wide temperature region. The corresponding values of the conductance varied from $3.31 \times 10^{-11} \Omega^{-1}$ up to $1.5 \times 10^{-8} \Omega^{-1}$, respectively.

Kutnjak *et al* [47] also reported measurements of temperature dependent electrical conductivity obtained on

native wet-spun calf thymus Li-DNA in a dc measuring field. Wet-spun oriented samples were prepared from calf thymus Li-DNA with a molecular weight of 10^7 (corresponding to a contour length of about 5 mm, or some 10^2 persistence lengths of 50 nm) by wet spinning and then drying. The wet spinning method allows for controlled production of sufficient amounts of highly microscopically oriented thin films by spooling DNA fibers that are continuously stretched during precipitation into an aqueous alcohol solution. The dried Li-DNA sheets of thickness about 3–4 mm and surface area between 10 and 20 mm^2 were then cut perpendicularly to the orientational axis of the DNA molecules into bulk samples of $6.4 \times 4.4 \times 3.4 \text{ mm}^3$ that were used in conductivity measurements. Electrodes were pressed on both sides of the sample. Quasistatic resistivity and I – V curve measurements were performed with a Keithley 617 programmable electrometer on samples kept in 75% relative humidity and on samples dried in a vacuum. They concluded that their measurements could be rather well described by the activated Arrhenius law, but based on the quality of the fits they did not exclude hopping. A strong temperature dependent conductivity was also observed, from 260 to 300 K, i.e. in a 40 K-wide temperature region.

As pointed out by one of the authors in a previous publication on DNA [10], the experimental values of the measured conductivity vary by many orders of magnitude within different temperature ranges, more or less wide. In section 4 we apply our theoretical approach to the data which are related to the wider ‘high temperature’ regions (I, II and III) in order to maximize the credibility of the fits. The data of Kutnjak *et al* [47] are excluded because they are referred to a very narrow temperature region about 40 K wide. By ‘high temperature’ regions we characterize those in which the measured conductivity shows a pronounced strong dependence, although this is strictly determined by the condition $\hbar\omega_0 \leq k_B T$ [24]. The low temperature region is characterized by a very weak temperature dependence of the conductivity.

4. Results and discussion

Figures 1, 2 and 3 show the $\ln \sigma$ versus $T^{-1/2}$ plots for these data, namely Tran *et al*'s (12 GHz) data (I) [14], Inomata *et al*'s data (II) [19] and Yoo *et al*'s (poly(dA)–poly(dT)) data (III) [15], respectively. The experimental data nicely follow the $T^{-1/2}$ law. Given that the strong temperature dependence of the measured conductivity can be equally nicely fitted using different exponential laws, as has been attempted in the past [14, 15], the quality of the fits does not necessarily guarantee the validity of our theoretical approach. However, our theoretical analysis allows the evaluation of $r_m^{h,cr}(T)$. The maximum hopping distance, $r_m^{h,cr}(T)$, and its T -dependence is analytically derived taking into account basic characteristics of the system under study, i.e. disorder, the polaronic character of the carriers and correlation effects. This makes the maximum hopping distance an important quantity for testing the reliability of our theory.

The value of $T_0^{h,cr}$ is determined from the slope of the $\ln \sigma$ versus $T^{-1/2}$ curves (equation (29)). Using equation (31)

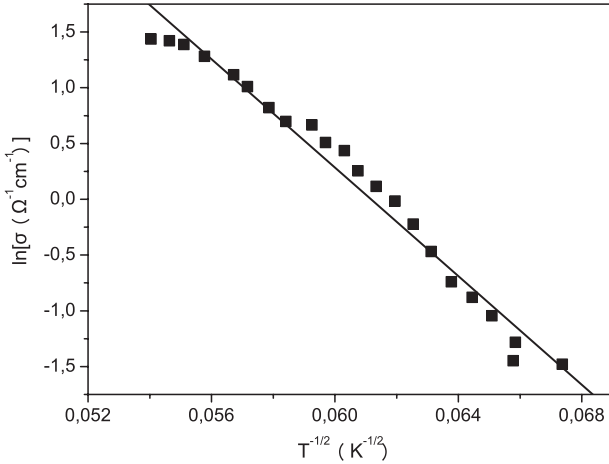


Figure 1. $\ln \sigma$ versus $T^{-1/2}$ plot of Tran *et al*'s (12 GHz) data [14] for λ -DNA.

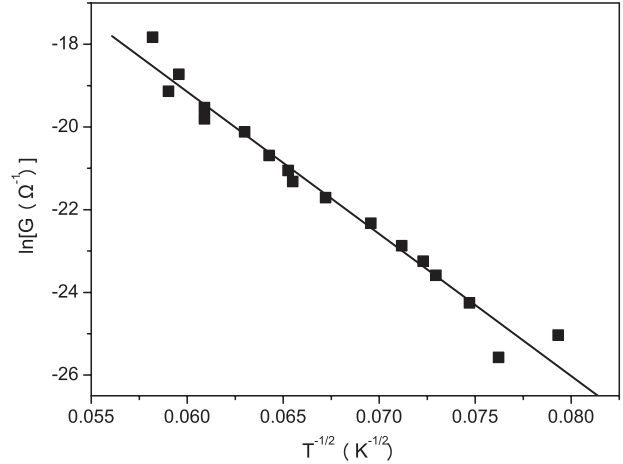


Figure 3. $\ln G$ versus $T^{-1/2}$ plot of Yoo *et al*'s data [15] for poly(dA)–poly(dT) DNA.

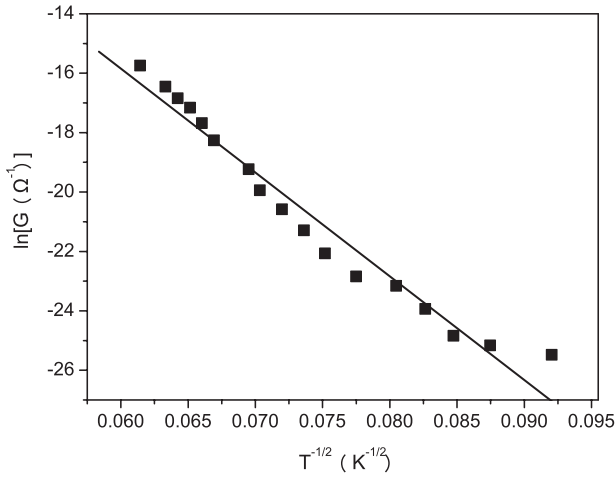


Figure 2. $\ln G$ versus $T^{-1/2}$ plot of Inomata *et al*'s data [19] for λ -DNA.

Table 1. Maximum hopping distance.

Exp. data	r_m^h	$r_m^{h,cr}$
I	(227 K) 11.40 Å (3 bp)	(227 K) 16.14 Å (5 bp)
	(342 K) 8.70 Å (2 bp)	(342 K) 13.15 Å (4 bp)
II	(118 K) 25.91 Å (8 bp)	(118 K) 32.13 Å (9 bp)
	(265 K) 14.81 Å (4 bp)	(265 K) 21.44 Å (6 bp)
III	(178 K) 18.8 Å (5 bp)	(178 K) 25.76 Å (8 bp)
	(306 K) 13.00 Å (4 bp)	(306 K) 19.65 Å (6 bp)

We notice that the relative magnitude of the maximum hopping distance, i.e. $r_m^h(\text{II}) > r_m^h(\text{III}) > r_m^h(\text{I})$, ignoring correlations, remains the same including correlations, as expected, for the lower and higher temperatures of the ‘high temperature’ region, i.e. $r_m^{h,cr}(\text{II}) > r_m^{h,cr}(\text{III}) > r_m^{h,cr}(\text{I})$.

Our results imply that as the temperature increases, shorter hops (or equivalently smaller impedances, cf equations (30) and (31)) contribute to the transport process, resulting in an increase in conductivity, in accordance with experiment.

Although until recently it was reported [37] that the hopping of small polarons over large distances across the DNA double helix is improbable, correlation effects make possible small polaron hops up to nine base pairs, at least for the experiments under study.

To our knowledge the only effort to interpret the experimental data based on a specific expression for the I – V characteristics [52] has been presented in [15]. This expression was borrowed from amorphous semiconductor theory. The lack of an analytical expression based on a transport mechanism appropriate for the specific system forced Yoo *et al* [15] to use the (fitting) parameter b to fit—as $I \sim bV$, the specific expression referred to in [52]—to their experimental data. According to the authors, the parameter b has a temperature dependence of unclear physical origin. The above probably resulted in an unconvincing attempt, as the authors [15] noticed, to interpret Tran *et al*'s data [14].

On the other hand the use of a simple Arrhenius-type formula by other workers to fit their experimental data seemed to be inadequate to account for important features of the actual

(for $\alpha^{-1} = 2 \text{ \AA}$ [53, 54]) we evaluate the maximum hopping distance, $r_m^{h,cr}(T)$, at the lower and higher temperatures of the ‘high temperature’ region.

For λ -DNA using Tran *et al*'s [14] data (I), we obtain $T_0^{h,cr}(\text{I}) = 59 \times 10^3 \text{ K}$, $r_m^{h,cr}(\text{I})(227 \text{ K}) = 16.14 \text{ \AA}$ (five base pairs), and $r_m^{h,cr}(\text{I})(342 \text{ K}) = 13.15 \text{ \AA}$ (four base pairs).

Respectively, for λ -DNA using Inomata *et al*'s [19] data (II), we obtain $T_0^{h,cr}(\text{II}) = 12.19 \times 10^4 \text{ K}$, $r_m^{h,cr}(\text{II})(118 \text{ K}) = 32.13 \text{ \AA}$ (nine base pairs), and $r_m^{h,cr}(\text{II})(265 \text{ K}) = 21.44 \text{ \AA}$ (six base pairs). The values for $r_m^{h,cr}$ obtained for λ -DNA for both experiments are mutually consistent given the temperature values in which the experiments were performed.

For Yoo *et al*'s [15] data (III), we obtain $T_0^{h,cr}(\text{III}) = 11.8 \times 10^4 \text{ K}$, $r_m^{h,cr}(\text{III})(178 \text{ K}) = 25.76 \text{ \AA}$ (eight base pairs), and $r_m^{h,cr}(\text{III})(306 \text{ K}) = 19.65 \text{ \AA}$ (six base pairs).

Table 1 shows the maximum hopping distance for both cases, i.e. for uncorrelated [10] and for correlated hopping at the lower and higher temperatures of the ‘high temperature’ region. The maximum hopping distance for Inomata *et al*'s data has also calculated for the uncorrelated case.

transport mechanism, and did not produce any significant information about the transport process. This is probably the reason for the lack of a simultaneous interpretation of the experimental findings [15, 14, 19] which show a similar behavior of the conductivity in DNA at high temperatures.

The approach presented in the present work is based on first principles, leading to analytical expressions for the conductivity as a function of the temperature and the maximum hopping distance. For this reason it does not need any adjustable fitting parameter because the responsible transport mechanism is described in detail. All three experiments are consistently analyzed.

As we pointed out in section 3, various factors affect the electrical properties of DNA. Tran *et al* [14], Inomata *et al* [19] and Yoo *et al* [15] measured the electrical conductivity of different DNA samples. Their data are for DNA samples of different length, different base pair sequences and different experimental settings. These differences do not seem to affect the qualitative behavior of the conductivity at high temperatures, which shows a similar strong T -dependence for all three experiments. We notice that although in these experiments the conductivity exhibits the same qualitative pronounced T -dependence, its value differs significantly for the samples under consideration within the relevant temperature ranges.

Here we have to note that our theoretical model takes into account, as we pointed out in section 3, only the basic characteristics of DNA, which makes it a potential candidate for application of the theoretical results. These characteristics, i.e. the small polaronic character of the carriers, the prevalence of the polaronic character of disorder [12] and the multi-phonon hopping type transport, could be attributed to all three DNA samples we deal with. Incorporating these characteristics in our theoretical analysis we produced an analytical expression for the temperature dependence of the conductivity, which seems to reproduce satisfactorily the experimentally observed qualitative behavior of the conductivity. The above remarks drive us to assert that the characteristics referred to in section 3, which are common for all three experimental samples, prevail over the specific characteristics of the individual DNA samples under study, and determine the qualitative behavior of the conductivity. It seems that the inclusion of the DNA site energies (there are indeed four types of sites), the specific configuration of bases, the length of the DNA sequence and other relevant factors in the theoretical analysis should be taken into account when we try to reproduce quantitatively the measured values of the conductivity of any particular DNA samples under study.

Finally, the specific influence of the cations(counterions) has to be incorporated in a detailed analysis. The DNA helix is stabilized by positively charged counterions which prevent the two strands from dissociating under the repulsion between the concentrated anionic phosphate groups [55]. Recent studies, using a variety of techniques, suggest that counterions may be more involved in DNA structure, with specific interaction sites [56, 57]. Indeed, although the bases are neutral overall, they have electron-rich groups that can form electronegative pockets potentially suited to

host cations. Although experimental reports suggest that the type of counterion affects the DNA structure, the nature of the structural effect remains obscure. Depending upon the concentration of the cations (counterions), their valency and the charge of the carrier (electron or hole), the cation(counterion)-charge interactions could affect the strength of the charge-'lattice' interaction, and, consequently, the magnitude of the mobility of the carrier.

5. Summary

In summary, we developed a theoretical model for the temperature dependence of the electrical conductivity when small polarons are transported in a disordered 1D environment at high (h) temperatures. Correlation (cr) effects were taken into account.

The theoretically obtained $\ln \sigma^{h,cr} \sim T^{-1/2}$ law satisfactorily reproduces the strong T -dependence of the conductivity reported for λ -DNA and for poly(dA)-poly(dT) DNA at high temperatures. The fits of this theoretical result with the experimental data permit the evaluation of the maximum hopping distances. The results indicate that correlation effects are probably responsible for large hopping distances in DNA samples.

Thus, correlated multi-phonon-assisted small polaron hopping across several base pairs of the DNA double helix could be a probable charge transfer mechanism responsible for the strong temperature dependence of the electrical conductivity of DNA measured at high temperatures.

The energetics of the base upon which the small polaron resides, the particular configuration and the length of the specific DNA sequences should be taken into account in a quantitative study of the measured conductivity.

Acknowledgments

The authors would like to express their appreciation for the referees' comments and suggestions which opened for them a new window to the understanding of DNA. Stimulating discussions with Dr M Tsetseri are also deeply appreciated.

This work was funded by the program KAPODISTRIAS (ELKE/National and Kapodistrian University of Athens).

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