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"Hopping Transport in 1D Chains (DNA vs. DLC)"

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Hopping transport in 1D chains (DNA vs. DLC)

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We discuss charge transport in one-dimensional organic solids (DNA and discotic liquid-crystalline glass (DLC)), focusing on the effects of static and dynamic disorder. In the presence of static disorder it can be shown that the temperature dependence of the low - field mobility is $\mu \propto \exp[-(T_0/T)^2]$, with characteristic temperature T_0 depending on the scale of the energy distribution of localized states responsible for transport. In the case of both static and dynamic disorder the situation is different. We obtain a temperature independent mobility in our molecular dynamics calculations in the case of large static and dynamic disorder compared to the energy overlap integral between the neighbouring sites. The theoretical results are in good agreement with experimental data.

1 Introduction It was already suggested in the 1960's that DNA is a possible candidate for a one-dimensional transport material because of the π-overlap between the neighbouring bases. Recent experiments have demonstrated a long-range charge migration along the DNA double helix, indicating that DNA can serve as a one-dimensional molecular wire. However, the actual magnitude of DNA conductivity as well as its physical mechanism is still under debate. A number of conflicting experimental results have been reported and a variety of theoretical models have been suggested [1-17], but a consensus on charge transport in DNA has not yet been reached. For example, it was published by different groups that DNA is an insulator [3,4], or a semiconductor [5,6], or has very good conduction properties [7], and there are even suggestions for a superconducting behaviour [8]. It is a fundamental task to understand charge transport mechanism along the DNA chain. It will enable us to better understand the damage and repair mechanism present in biological systems. In addition, we can get a better insight into the possible electronic and medical applications. Charge (electron or hole) transport in DNA can be modelled as a quasi-one-dimensional transport along the helical chain. This transport takes place along the main building elements of DNA (guanine, cytosine, thymine, and adenine), which can be considered as sublattice sites for the charge transport. In such a system, static and dynamic disorder can play a crucial role.

Numerous chemical studies have shown that after inserting a charge carrier into a donor-DNA-acceptor system, the carrier moves along the DNA chain via hopping between DNA bases [18]. For example, holes tend to hop via guanine bases, which provide essentially lower energies for such carriers compared to other DNA bases. The rate of hopping processes strongly depends on the number of adenine-thymine bases bridging the neighbouring guanines for short bridges evidencing the tunnelling hop-

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ping transitions. Unfortunately, being based on the reaction yields and not on the direct measurements of the transient times, the study of transport phenomena in such "chemistry at a distance" experiments does not reveal much physical information. Therefore, studies of hopping transport in organic one-dimensional systems have been concentrated so far mostly on systems which are widely believed to be similar to the DNA chain, namely, on discotic liquid-crystalline glasses (DLC) [10,19,20]. Both DNA and DLC consist of quasi-one-dimensional chains of flexible organic units separated by distances of about 0.35 nm. In contrary to DNA chains, the DLC systems allow a straightforward experimental study of transport phenomena including the dependencies of the carrier mobility on essential parameters like temperature and electric field in wide ranges of the corresponding parameter values.

Columnar discotic liquid crystalline glasses have recently caused a particular interest because of their potential application for electrography and for transport materials in light-emitting diodes[21]. The proximity (0.35 nm) of molecular units leads to a strong overlap of electron wave functions on neighbouring units, which can provide high charge carrier mobility values favourable for technical applications. These systems enable researchers to test different transport approaches. Regarding the temperature dependence of the mobility, DLC can be separated into two groups. In the first group, materials have temperature dependent mobility proportional to $\mu \propto \exp[-(T_0/T)^2]$ with some characteristic temperature T_0 [22,23]. This type of behaviour of the mobility can be described in the framework of a hopping theory in a quasi-one-dimensional chain [24-26]. To the second group belong materials which exhibit almost temperature independent mobilities [27]. This latter behaviour cannot be described by simply assuming the presence of static disorder and a dynamic disorder should be also taken into account.

In this paper, we show principles of numerical algorithms and analytic calculations suitable for describing the charge transport in quasi-one-dimensional systems, where the effects of static and dynamic disorder play an important role. This paper is organised as follows. In the next section the effects of static disorder are studied. Section 3 describes the effects of both static and dynamic disorder. In section 4 their relevance to charge transport in DNA and DLC systems is discussed.

2 Static disorder It was shown that in chain systems, such as DLC, the charge transport is extremely anisotropic. The mobility along the chains is more than three orders of magnitudes larger than in the perpendicular direction. This allows one to model the transport in a quasi-one-dimensional environment. Experimentally observed dependences of the conductivity on the frequency, on the strength of the applied electric field, and on the temperature evidence that an incoherent hopping process is the dominant transport mechanism in such materials [22,23,28]. It is widely believed that energy levels which are responsible for charge transport in such systems have a Gaussian density of states

$$d(\varepsilon) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right), \qquad (1)$$

where σ is the width of the distribution[21]. In these quasi-one-dimensional chains the charge carriers hop via molecular sites. The transition rate from the occupied localised state i to an unoccupied site j is usually described by the Miller-Abrahams rates $\Gamma_{ij} = \Gamma_0 \exp(-2R_{ij}/\alpha) \exp\left(-\frac{\varepsilon_j - \varepsilon_i + |\varepsilon_j - \varepsilon_i|}{2kT}\right)$, where Γ_0 is the attempt-to-escape frequency, R_{ij} is the distance between sites i and j, k is the Boltzmann constant and ε_i and ε_j are the corresponding site energies.

The temperature and electric field dependences of the mobility in such a system were extensively studied by Cordes *et al.* [24-26]. It was shown by analytical calculations and Monte Carlo simulations that the temperature dependence of mobility has a form of

$$\mu(T) = \mu_0 \exp\left(-A\left(\frac{\sigma}{kT}\right)^2\right), \tag{2}$$

with some coefficient A in a good agreement with experiments [22,23]. Figure 1 shows such a strong exponential dependence on temperature both for analytical calculations and for Monte Carlo simulations. It was found that at large temperatures, the nearest neighbour hopping is the dominant process in these systems. At lower temperatures tunnelling to second-, third-nearest neighbours, etc. gets more and more important. This affects the value of the coefficient A in Eq.(2), which changes from 1 (at large temperatures) to $(n+1)/2n$ (low temperatures), where n is the n-nearest neighbour essential for hopping processes. However, in the experimentally studied systems this change is only relevant for A being between about 0.7 and 1 [26].

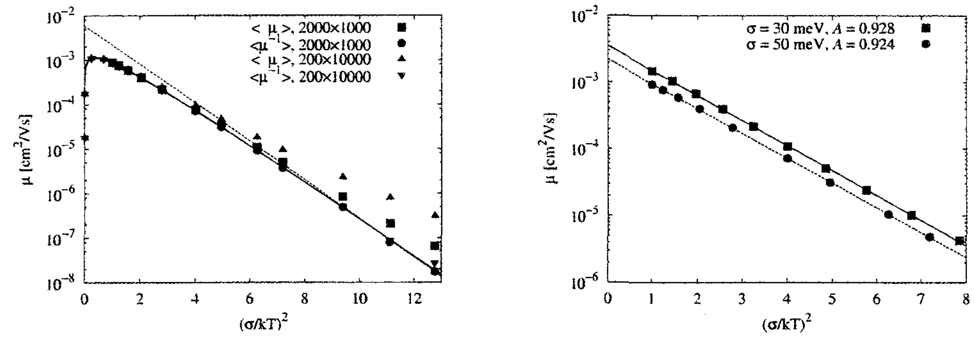

Fig. 1 In the left figure, the temperature dependence of the low-field mobility for $\sigma = 50$ meV is shown. Different symbols show different types of averaging and different system sizes. Solid line represents the solution for infinite chain. Dashed line is a guide for the eyes with a slope equal to -1. In the right figure, the results of Monte Carlo simulations are shown.

Much attention has been paid in the recent years to the dependence of the drift mobility in organic systems on the electric field. In particular, the reported increase of the drift mobility with decreasing field [21,29-31] at low electric fields caused a lot of discussions in the scientific literature. In their theoretical calculations, Cordes *et al.* [24] have shown that this increase at $F \rightarrow 0$ was erroneously interpreted and it can be explained as follows. In the experiments the mobility is calculated by $\mu = b/(Ft_{tr})$, where b is the length of the sample, F is strength of the electric field and t_{tr} is the transit time. If this expression is used in the theoretical calculations the above mentioned anomaly can be observed [24]. Figure 2 illustrates such an increase of the mobility at low fields. However, the charge carrier would pass through the system even at zero electric field solely due to diffusion. Therefore, at very low fields it is more appropriate to calculate the mobility via the diffusion formula using the Einstein relation $\mu = (eD)/(kT)$, with calculating the diffusion constant by $D = b^2/2t_{tr}$. In Fig. 2 it is shown that this latter calculation coincides at low electric fields with the results for the mobility calculated by drift formula at higher fields. This agreement between two approaches confirms the application of the diffusion formula at $F \rightarrow 0$. It was therefore concluded that the anomalous behaviour of the mobility at low electric fields found in the experiments is only an artefact and has no physical meaning. The same conclusion has been supposed earlier on the basis of experimental studies of the mobility in organic semiconductors at low electric fields [32], though it could not be claimed for sure before the theoretical calculations confirmed this result [24].

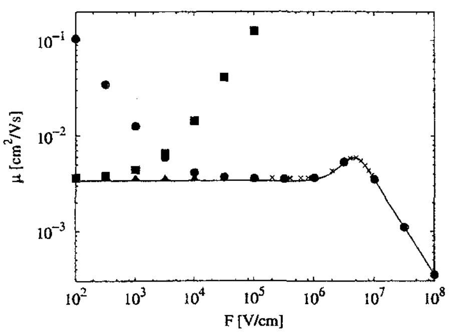

Fig. 2 Field dependence of the carrier mobility at $kT = 25$ meV. The solid line represents the exact solution for infinite chain. Data shown by circles and squares were calculated in finite systems via drift and diffusion formulas, respectively. Crosses show the results of the Monte Carlo simulation.

3 Static and dynamic disorder The results with static disorder are really important, because they are able to explain such puzzling features as the field dependence of the mobility and the temperature dependence at low temperatures. However, in some DLC the temperature dependence of the mobility is not exponential and temperature independent mobility values were reported above room temperature [27]. In such systems dynamic disorder also should be taken into account. Palenberg *et al.* used a model in which only dynamic disordered effects were considered [33]. However, their model only provides temperature independent parts of the mobility in a small temperature range.

We used a tight-binding model Hamiltonian for describing static and dynamic energy disorder in organic solids. We consider a one-dimensional chain where every site belongs to a molecular sequence of the related material. Following Vekhter *et al.* [34], a charge carrier is generated at a particular site. The motion of this charge carrier is determined by the Hamiltonian

$$H = H_c + H_{ph} + H_{c-ph} \, . \tag{3}$$

The first part H_c describes the on-site energies and the first-neighbour hopping terms

$$H_c = \sum_n \varepsilon_n a_n^+ a_n - \sum_n \beta (a_n^+ a_{n+1} + a_{n+1}^+ a_n) \, , \tag{4}$$

where n is the site label in the chain, $a_n^+ (a_n)$ denotes the creation (annihilation) operator of the charge carrier, the variables ε_n correspond to the on-site energies (static disorder), and β is the energy overlap integral between neighbouring sites. The motion of the site molecules (phonon bath) is described by a classical harmonic oscillator Hamiltonian

$$H_{ph} = \sum_n \{ \frac{p_n^2(t)}{2M} + \frac{1}{2} M\omega^2 [x_{n+1}(t) - x_n(t) - x_{eq}]^2 \} , \tag{5}$$

where $p_n(t)$ and $x_n(t)$ are the momenta and the coordinates of the molecular sites, M is their mass , x_{eq} is the equilibrium distance between the sequential sites on the chain, and ω is the vibration frequency. The interaction of a charge carrier with molecular sites (electron-phonon interaction) in the chain is described by the

$$H_{c-ph} = \sum_n g\left(x_{n+1}(t) - x_{n-1}(t) - 2x_{eq}\right) a_n^+ a_n \,, \tag{6}$$

where g is the coupling constant. The last equation provides the time dependent site energy values ($\tilde{\varepsilon}_n(t)$), which fluctuate around the static disorder values: $\tilde{\varepsilon}_n(t) = \varepsilon_n + g\left(x_{n+1}(t) - x_{n-1}(t) - 2x_{eq}\right)$. The wave function of the charge carrier in the above second quantization formalism is $|\Psi(t)\rangle = \sum_n c_n(t)|n\rangle$.

We insert the particle into the system at time $t = 0$, by taking the coefficients in this expansion as $c_0(t = 0) = 1$ and $c_{n \neq 0}(t = 0) = 0$. Then the time evolution of the system can be described by calculating the new charge carrier wave function at time $t + \Delta t$ using the electronic part of the total Hamiltonian (Eq. (3)) $i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle$, followed by the calculation of the positions and velocities of the oscillators at time $t + \Delta t$ with the help of the effective potential derived from the electronic contribution. Once it is done, the procedure can be repeated. To study the transport, we calculated the mean square displacement of the charge carrier by $\langle \Psi(t)|n^2|\Psi(t)\rangle = \sum_n |c_n(t)|^2 n^2$. From this quantity one can evaluate the diffusion constant and the mobility can be calculated from the diffusion constant via the Einstein relation.

In our computer simulations before the injection of the charge carrier into the system, the molecular complex was equilibrated by the following method. At the starting stage, every molecular site was placed at its equilibrium position. The velocities were distributed according to a given temperature by the Maxwell-Boltzmann distribution. Then the system was let to evolve for 2.5 ps. After this time delay we had an equilibrated system with kinetic energy fluctuating at half of the starting temperature. We took this kinetic energy as the temperature of the system. For the next step, a charge carrier was generated in the middle of the chain at $t = 0$. The time evolution of the wave function was approximated by the symmetric Cayley formula:

$$|\Psi(t + \Delta t)\rangle = \exp[-iH(t)\Delta t]|\Psi(t)\rangle \approx \frac{1 - \frac{1}{2} iH(t)\Delta t}{1 + \frac{1}{2} iH(t)\Delta t} |\Psi(t)\rangle . \tag{7}$$

The time step Δt was chosen as 0.1 fs. We checked that smaller time steps do not bring any effect to the physical picture. The separation distance between the molecular sites was 0.35 nm. Following previous studies [19,34], we have chosen the M mass of the oscillators as 60 proton mass, the oscillation frequency ω as $1.4 \cdot 10^{13}$ Hz, and the coupling constant g as 5.15 eV/nm. The charge carriers were injected in the middle of the chains. We checked that no size effects are present by choosing long enough chains during the 150 ps long simulations. Our systems typically consisted of 1001 sites and the averages were calculated over 100 realisations of each system. In our computer simulations the site energies ε_n were distributed according to a Gaussian formula (Eq. (1)), with σ = 0, 25, 50, and 75 meV. The overlap parameter β was taken as 10, 15, and 25 meV. This choice leads to the range of the ratio σ / β between 1.0 and 7.5.

Figure 3 summarises our results showing the temperature dependence of the mobility in systems having large static disorder (σ = 75 meV) with the overlap parameter β changing from 10 to 25 meV. The results clearly show that dynamic disorder can really suppress the strong temperature dependence of the mobility calculated in the systems with only static disorder. In a wide temperature range we found almost temperature independent mobility values if the *σ/β* > 4. However, if this ratio gets smaller, the typical temperature dependence can be described as *1/T*.

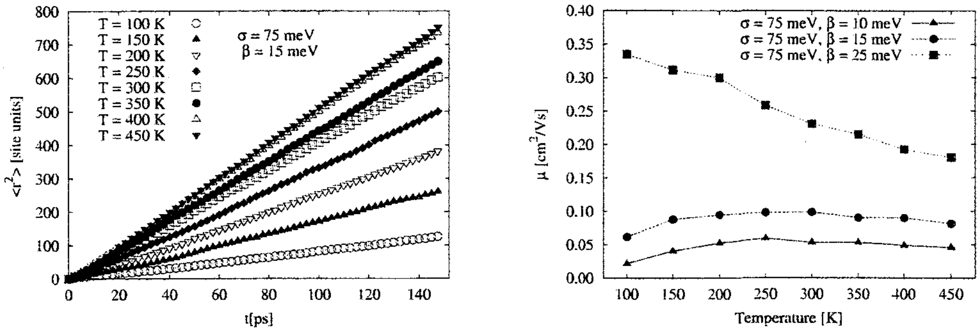

Fig. 3 In the left figure, the mean square displacement is shown for different temperatures for parameters σ = 75 meV and β = 15 meV. In the right figure, the temperature dependence of the mobility with static and dynamic disorder is shown.

4 Discussion Organic disordered systems (such DLC and DNA) can be very much different from inorganic disordered solids. It is believed that in the latter materials only static disorder is dominant, whereas it is "expected" that in organic systems dynamic disorder also plays a crucial role for transport and other physical properties. Both DLC and DNA have flexible organic units along the chain axis. In the previous two sections we have presented theoretical descriptions of different approaches to such quasi-one-dimensional systems. It was shown that the temperature dependence of the mobility can change drastically from an exponential to an almost temperature independent behaviour, depending on the presence on dynamic disorder.

Chemical studies have shown that there is hopping in DNA. In such experiments, small donor-DNA-acceptor bridges are constructed and the transport properties were extracted from reaction yield measurements. Unfortunately, in those experiments the dependence of the transport properties on temperature or electric field has not been studied. Physical experiments tried to address such issues, but the reported results are contradictory and almost each group reported different transport properties. The difficulty lies in the fact that the transport properties depend on several circumstances, which are really hard to control in the experiments. Aiming and hoping in the future to apply algorithms to DNA molecules, we concentrated so far on DLC, a system similar to DNA, in which interesting experiments are abundant.

Surprising and interesting results were reported for DLC. In one set of experiments strong exponential temperature dependence of mobility was reported, whereas there are other systems where temperature independent mobility values were measured. We claim that these variations can be explained by the strength of dynamic disorder in different systems. Our molecular dynamics simulations show that dynamic disorder can suppress the exponential temperature dependence of the mobility, which was found in the case of "pure" static disorder. Therefore, we suggest that in these latter systems (with strong exponential dependence on temperature) the effect of dynamic disorder on transport is small. On the other hand, in systems where temperature independent mobility was reported the effect of dynamic disorder seems to be crucial.

5 Conclusion The temperature dependence of mobility in quasi-one-dimensional organic systems, such as discotic liquid-crystalline glasses (DLC), has been studied with taking into account static and dynamic disorder effects. We have shown that in the case of static disorder the temperature dependence of the mobility is exponential. In the case of static and dynamic disorder temperature independent mobility values can be obtained with reasonable parameters. Speculating about the strong structural similarity between DLC and DNA, we believe that our theoretical approach would also be valid for the description of charge carrier transport in DNA molecules.

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