On the Modeling of the Charge Transfer along 1-D Molecular Chain at T=300K

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Holstein Hamiltonian averaged by state |Ψ⟩

$$\hat{H} = \sum_{n,k} \nu_{nk} |n\rangle\langle k| \qquad |\Psi\rangle = \sum_{n} b_n(\tilde{t})|n\rangle \qquad n = 1, \ldots, N$$

$$H = T + U + \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle =$$

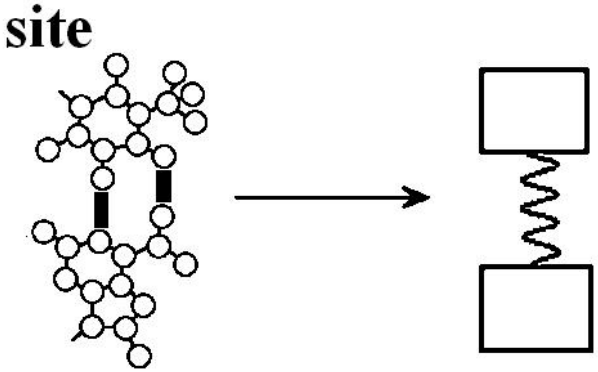
$$= \frac{1}{2}\sum_{n=1}^{N} M\dot{u}_n^2 + \frac{1}{2}\sum_{n=1}^{N} K u_i^2 + \sum_{m \neq n} \nu_{mn} b_m b_n^* + \sum_{n} \nu_{nn} b_n b_n^* + \sum_{n} \alpha' u_n b_n b_n^*.$$

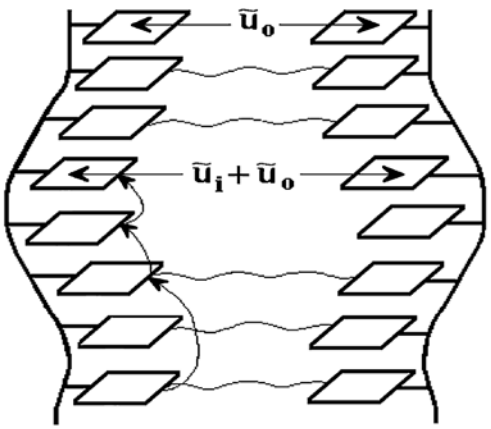
$b_n(t)$ is the probability amplitude describing the charge evolution on the site n.

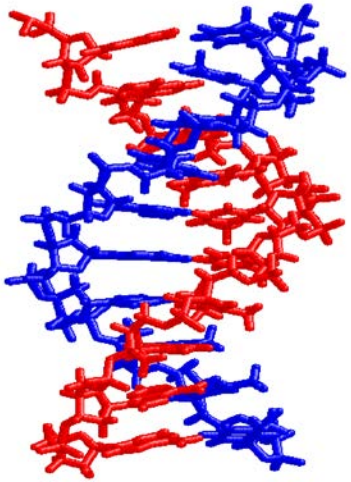
$u_n(t)$ is intrasite oscillations near the mass center

Probability distribution of the charge affects the movement of classical sites, and site displacement changes the probability of charge localization on it

DNA model







Nucleotide pair as a site

Sites move in a plane perpendicular to the DNA helix direction

Excess electron or hole (quantum particle) migrates along chain of classical sites.

Equations of motion

$$i\hbar\frac{db_n}{d\tilde{t}} = (\alpha_n{}^0 + \alpha'_n\tilde{u}_n)b_n + \nu_{n,n+1}b_{n+1} + \nu_{n,n-1}b_{n-1},$$

$$M_n\frac{d^2\tilde{u}_n}{d\tilde{t}^2} = -K_n\tilde{u}_n - \gamma_n\frac{\tilde{u}_n}{d\tilde{t}} - \alpha'_n|b_n|^2 + \tilde{\mathcal{A}}_n(t),$$

$$\langle\tilde{\mathcal{A}}_k(t)\rangle = 0, \quad \langle\tilde{\mathcal{A}}_k(t)\tilde{\mathcal{A}}_n(s)\rangle = \delta_{kn}\delta(t-s)2k_B\mathrm{T}\gamma_k,$$

variables: b_n – probability amplitude of finding the charge on the n-th site ,

u_n – displacement of n-th site from its equilibrium,

$n = 1, \ldots N,$

T –temperature of thermostat

Computer simulations

One sample is trajectory of the system with its own random time-series $\{A_n(t)\}$ and from its initial data

E.g., displacements and velocities of sites correspond to temperature prescribed

$$\langle \tilde{u} \rangle = 0, \quad \langle \tilde{v} \rangle = 0, \quad \langle \tilde{u}\tilde{v} \rangle = 0,$$

$$\langle \tilde{u}^2 \rangle = k_B \mathrm{T}/m\omega^2, \quad \langle \tilde{v}^2 \rangle = k_B \mathrm{T}/m$$

and the charge is localized at n-th site – donor:

$|b_n(t{=}0)| = 1$, other $|b_k| = 0$

Set of samples

There exists natural parallelism when solving these equations. We calculate each sample (the dynamics of the charge distribution from the different initial conditions and with different values of the random force) on a single node, using MPI to collect data at the master node, and averaging by ensemble the time-dependences:

Probability of charge localization at *n*-th site

$$\langle P_n(t)\rangle = \langle |b_n(t)|^2 \rangle$$

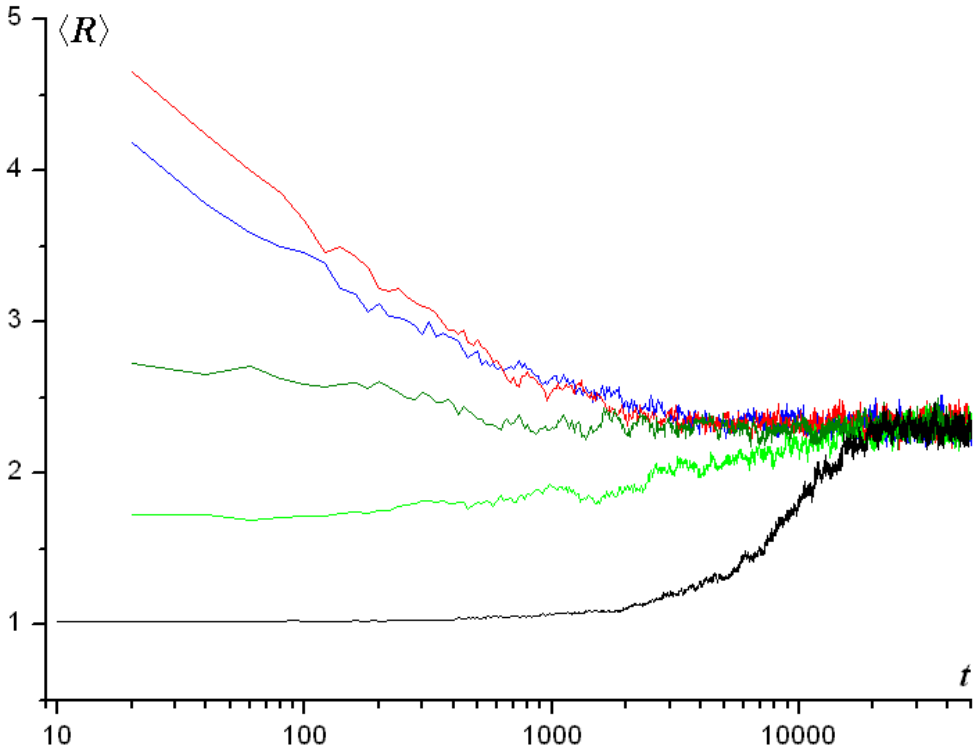
Total energy of the system

$$\langle E_{tot}(t)\rangle = \left\langle \eta \sum b_n b^*_{n\pm1} + \frac{1}{2}\sum v_n^2 + \frac{\omega^2}{2}\sum u_n^2 + \chi \sum u_n b_n b^*_n \right\rangle$$

Parameter of delocalization

$$\langle R(t)\rangle = \left\langle \frac{1}{\sum_n |b_n(t)|^4} \right\rangle$$

Evolution to the thermodynamic equilibrium state



Dynamics of $\langle \boldsymbol{R}(\boldsymbol{t}) \rangle$, calculated from different initial distribution of the charge. The bottom (black) curve represents calculation from the initial ‘polaron distribution’. The upper (red) curve – from uniform initial distribution of the charge over all the sites.

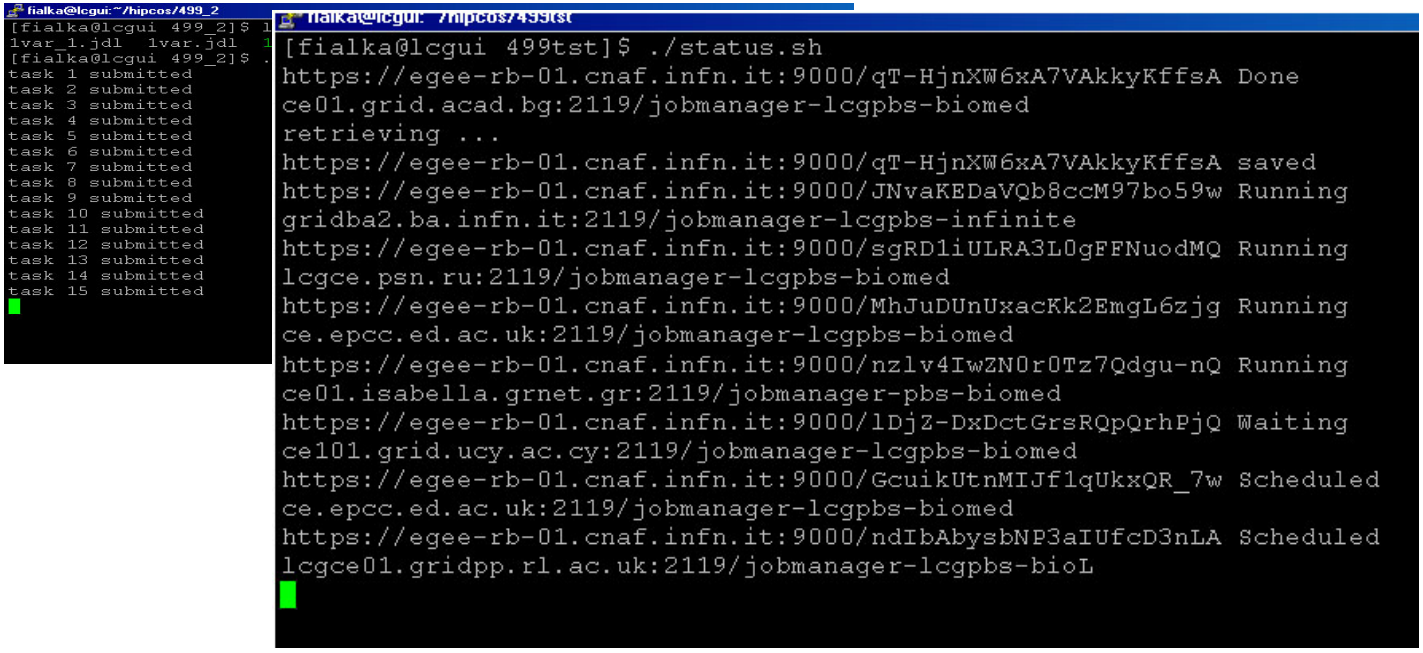
Each curve is the average on 50 samples

Computations on distributed resources

For adaptation to distributed computing, original program was divided into 2 parts.

The first program calculates one sample.

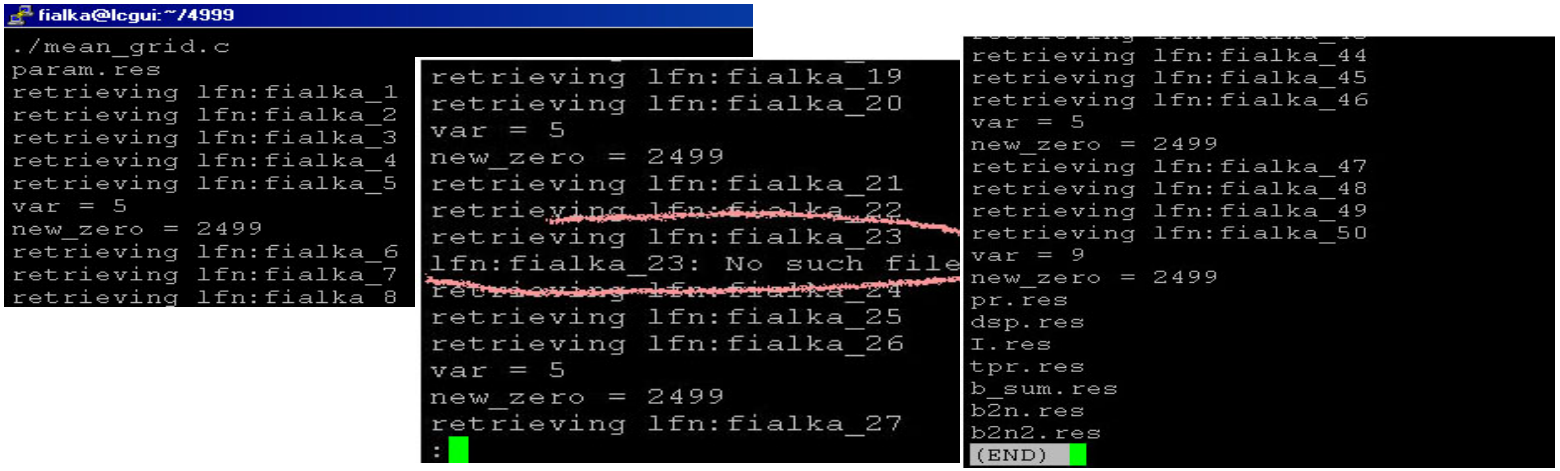
Using special script many copies of the program run with the same parameters and random initial data. Finally the files of results are compressed and transmitted to a predefined SE.



Averaging of calculations

After calculating enough number of samples, the second program runs. It must calculate average values.

A special script is sent to be calculated on WN. This WN takes from SE files with results of samples in series of 10 items, for every series the averaging program runs. At the same time if for some reason output file of one realization is absent or defective, it is ignored, and the next output file is taken. To files obtained the same program of averaging applies again.



Experiments on the charge transfer along DNA fragments

Hole transfer from guanine G (donor) to guanine triplet GGG (acceptor), separated by adenine-thymine (A-T) bridges of various lengths

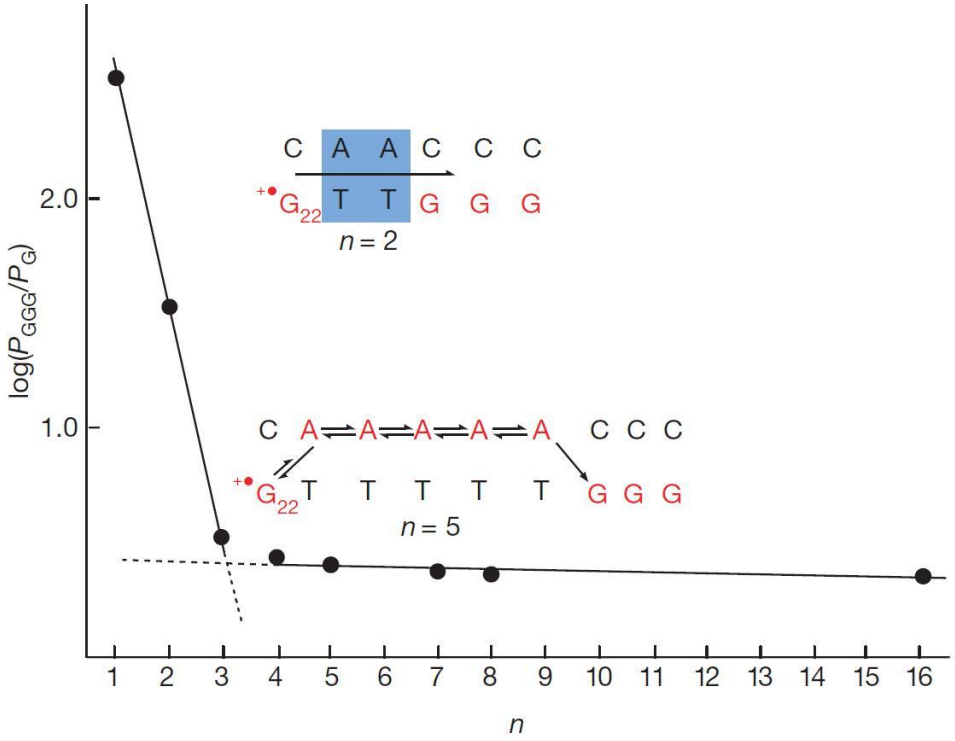


Fig. from: B. Giese et al, *Nature*, 412, 318 (2001)

The rate of charge transfer between donor and acceptor decreases with increasing bridge – for short fragments

For long bridge – the transfer rates exhibit only a weak distance dependence

Parameter values

are taken from literature data

oxidation potential		
	α^0, eV	η_{nn}
G	1.24	0
A	1.69	6.84
T	1.9	10.
C	1.9	10.

Electronic coupling matrix elements					
	$\nu_{n\,n+1}$, eV	$\eta_{n\,n+1}$		$\nu_{n\,n+1}$, eV	$\eta_{n\,n+1}$
GG	0.084	1.276	GT	0.137	2.081
TT	0.158	2.4	TG	0.085	1.291
AG	0.049	0.744	GA	0.089	1.352
AA	0.030	0.456	CA	0.029	0.441

$\tau = 10^{-14}$ sec,

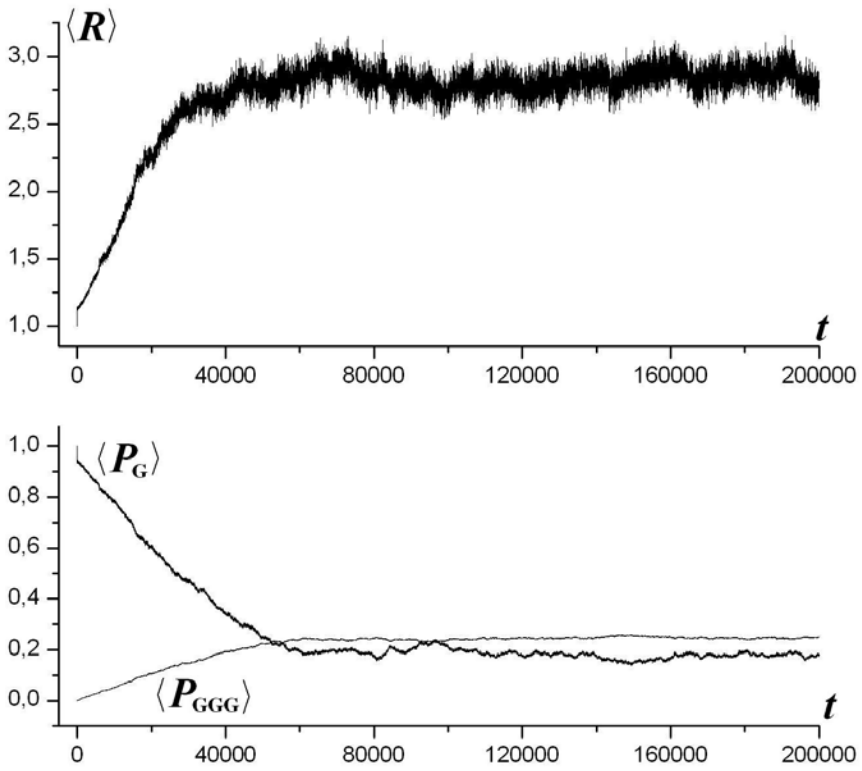
$M_n = 10^{-21}$ g

$\varpi \approx 10^{12}$ Hz $\quad (\omega = 0.01)$ $\quad 0 \le \alpha' \le 0.3$ eV /Å

J. Jortner, M. Bixon, A.A. Voityuk, N. Rosch (2002) J. Phys. Chem. A **106**, 7599-7606.

G.B. Schuster (2000) Acc. Chem. Res. **33**, 253-260.

Simulation experiments



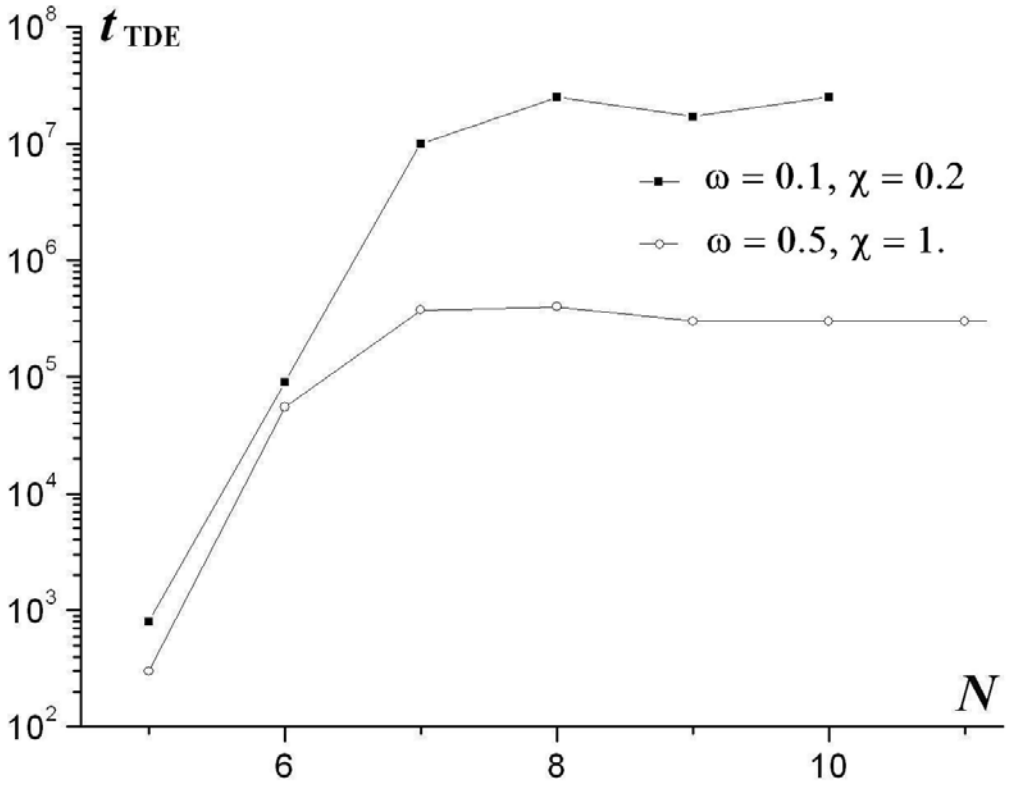
$\langle R(t)\rangle$ (top) and average probability on donor $\langle P_G(t)\rangle$ and on acceptor $\langle P_{GGG}(t)\rangle$ (bottom) for GAAGGG. T=300K

Time interval t_{TDE} from the initial state “the charge is localized at the donor G” to the attainment of the thermodynamic equilibrium state t_{TDE} ~ 60000

Modeling of charge transfer in GA…AGGG chains at T=300K

The length of the chain *N* varies from 5 (i.e. GAGGG – the bridge of one A) to 100 (i.e. GA. . .AGGG with 96 adenines).

For each *N* we have calculated the average for 100 samples on time interval of reaching the TDE state.



Experiments and Simulation Results

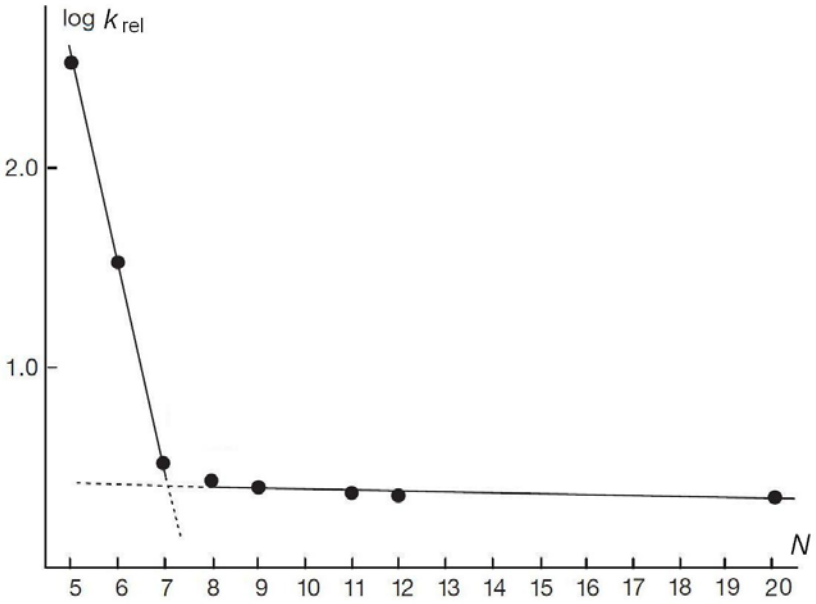
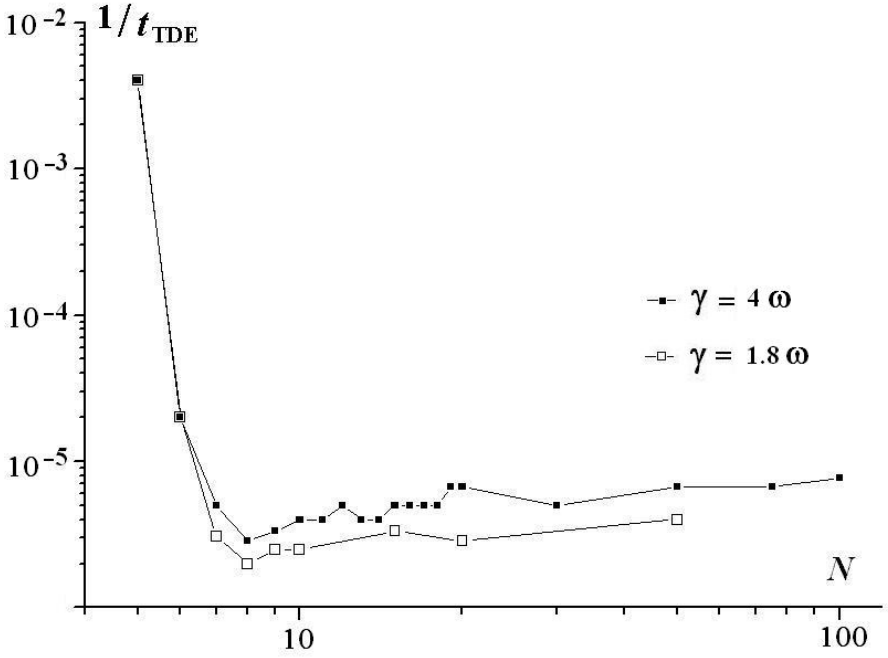


Fig. from: B. Giese et al, Nature, 412, 318 (2001)



Dependencies of the transfer rate $1/t_{TDE}$ on the chain length N for different friction coefficient

Conclusion

In biophysical experiments, it was found that for short chains ($N < 9$), lengthening the bridge on one site reduces the relative charge transfer rate by an order of magnitude. For chains with $N \geq 9$, the relative transfer rates are approximately constant.

Based on the Holstein model with Langevin term, computational modeling demonstrates that the time intervals of charge transfer from initial localization on donor to thermodynamic equilibrium state have a qualitative similar dependence on N.

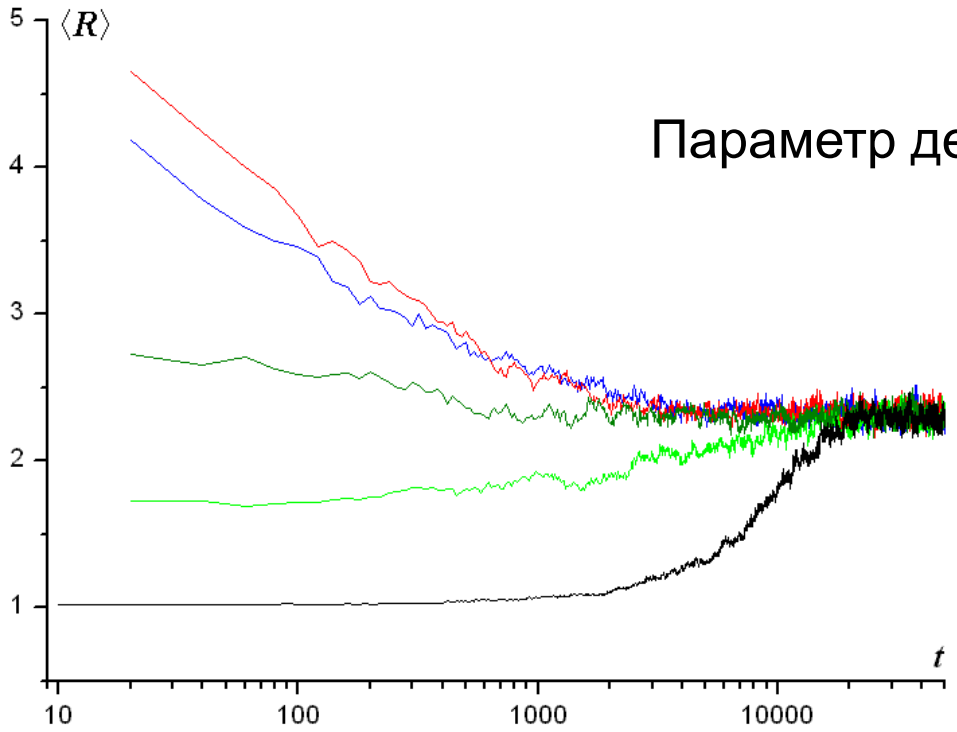
It can be assumed that (similarly to the case of homogeneous chains) in short chains the charge is in the polaron state, and in long chains the charge is delocalized, and the charge transfer from the donor to the acceptor occurs by different mechanisms.

Thank you for attention!

Термодинамические параметры

Полная энергия системы

$$\langle E_{tot}(t)\rangle = \left\langle \eta \sum b_n b^*_{n\pm1} + \frac{1}{2}\sum v_n^2 + \frac{\omega^2}{2}\sum u_n^2 + \chi \sum u_n b_n b_n^* \right\rangle$$



Параметр делокализации $\langle R\rangle = \left\langle \frac{1}{\sum |b_n|^4} \right\rangle$

Начальные данные:
Равномерное распределение (верхняя кривая)
полярон (нижняя кривая)

$\langle R(t)\rangle$, выход на состояние термодинамического равновесия

Stationary solution, T=0

$$i\dot{b}_n = \eta(b_{n-1} + b_{n+1}) + \chi u_n b_n,$$

$$0 = -\omega^2 u_n - \chi\,|\,b_n\,|^2 \quad \Rightarrow \quad u_n = -\frac{\chi}{\omega^2}\,|\,b_n\,|^2$$

$$b_n = r_n \exp(iWt)$$

$$-W\, r_n = \eta(\, r_{n-1} + r_{n+1}) - (\chi/\omega)^2\; r_n^3 \qquad n = 1,\ldots,N$$

$$\sum r_n^2 = 1$$

Systems with parameters $(\eta,\chi,\omega)\{I\}$ and $(\eta,C\chi,C\omega)\{II\}$ have the same steady-state solutions $\{r_1,\ldots,r_N,W\}$ (but $u_{n\{I\}} \neq u_{n\{II\}}$) and the same energy values

T ≠ 0. Partition function

$$Z = C_1 \cdot \int_{\Omega} \exp\left(-\frac{1}{C_2 T} E(b_n, b_n^*, u_n, v_n) \right) db_1 \cdots du_n \cdots dv_N$$

$$E = \eta \sum b_n b_{n\pm1}^* + \frac{1}{2} \sum v_n^2 + \frac{\omega^2}{2} \sum u_n^2 + \chi \sum u_n b_n b_n^*$$

$$\Omega = \mathrm{R}^{2\mathrm{N}} \times \mathrm{S}_{2\mathrm{N}} : u_n \in (-\infty; +\infty),\ v_n \in (-\infty; +\infty)\ ,\ \Sigma_n (b_n b_n{}^*) = 1$$

$$\langle E \rangle = \frac{\int_{\Omega} E \cdot \exp(-E(b, b^*, u, v) / C_2 T) dw}{\int_{\Omega} \exp(-E(b, b^*, u, v) / C_2 T) dw}$$

Total energy

Substitution $u_n \mapsto U_n = \omega u_n + \frac{\chi}{\omega} |b_n|^2$

$$\left\langle E_{tot} \right\rangle = NC_2T + \left[\int_S \exp\left(-\frac{F}{C_2T} \right) ds \right]^{-1} \cdot \int_S F \exp\left(-\frac{F}{C_2T} \right) ds$$

where $S = \left\{ \sum_{n=1}^{N} |b_n'|^2 = 1 \right\}$ and

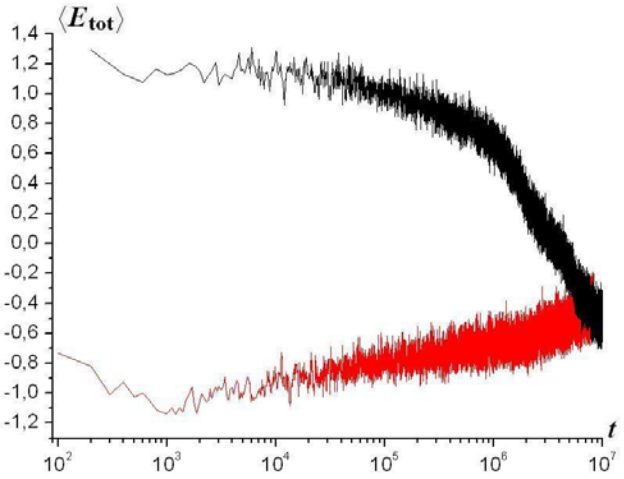
$$F = \eta \sum (b_n b_{n+1}^* + b_{n+1} b_n^*) - \frac{1}{2} \frac{\chi^2}{\omega^2} \sum |b_n|^4$$

For systems{I} (η,χ,ω) и {II} ($\eta,C\chi,C\omega$)

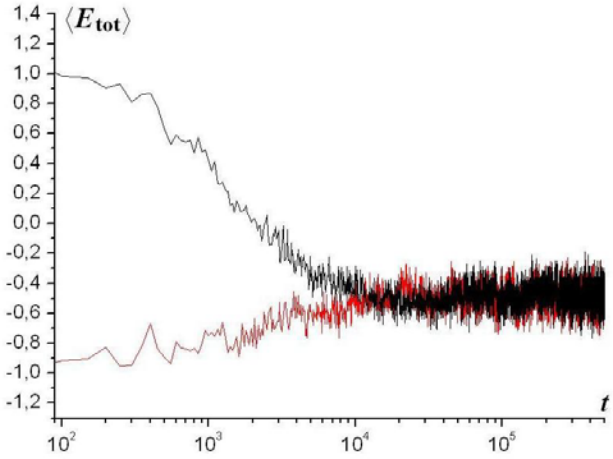
$$Z_{\{I\}} = \left(\frac{1}{C} \right)^N Z_{\{II\}} \quad \text{and} \quad \left\langle E_{\{I\}} \right\rangle = \left\langle E_{\{II\}} \right\rangle, \left\langle R_{\{I\}} \right\rangle = \left\langle R_{\{II\}} \right\rangle, \ldots$$

Tests for $\chi/\omega = 2$

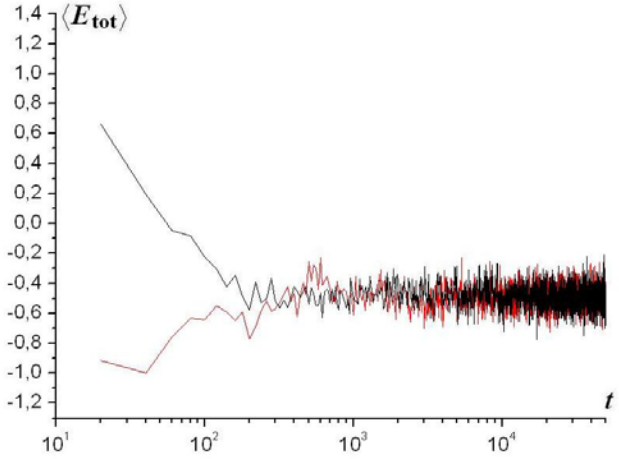
averaging over 50 samples



$\omega = 0.01$, $\chi = 0.02$ (DNA)



$\omega = 0.1$, $\chi = 0.2$



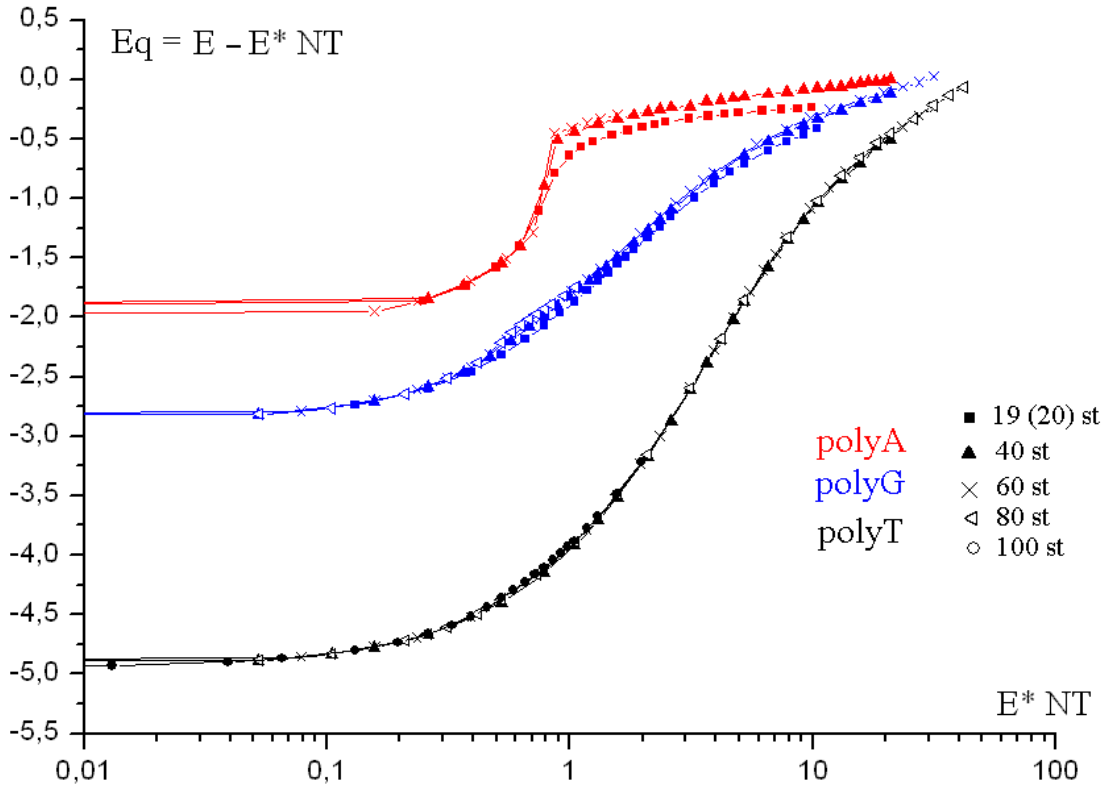
$\omega = 0.5$, $\chi = 1.$

χ/ω=const.

Time intervals of evolution to thermodynamic equilibrium are different,

calculated values are close to each other.

Homogeneous chains. Dependence of electronic part of energy on the thermal energy.



Charge distribution (polaron or delocalized state) in thermodynamic equilibrium state depends not only on the temperature, but also on the length of the chain

Homogeneous chains in TDE