



Temperature dependence of electronic heat capacity in Holstein model of DNA



N. Fialko*, E. Sobolev, V. Lakhno

Institute of Mathematical Problems of Biology RAS, Pushchino, Russia

ARTICLE INFO

Article history:

Received 26 December 2015

Accepted 27 February 2016

Available online 2 March 2016

Communicated by C.R. Doering

Keywords:

DNA

Langevin equation

Thermodynamic quantities

Polaron

ABSTRACT

The dynamics of charge migration was modeled to calculate temperature dependencies of its thermodynamic equilibrium values such as energy and electronic heat capacity in homogeneous adenine fragments. The energy varies from nearly polaron one at $T \sim 0$ to midpoint of the conductivity band at high temperatures. The peak on the graph of electronic heat capacity is observed at the polaron decay temperature.

© 2016 Elsevier B.V. All rights reserved.

The problem of how a charge, or energy is transferred in molecular chains is of great interest for biology and nanobioelectronics – a new rapidly developing discipline which combines achievements of nanoelectronics and molecular biology. One of the central problems of nanobioelectronics deals with creation of molecular nanowires and their circuits based on synthesized nucleotide chains. Therefore the study of conducting properties of DNA molecules is of profound interest [1–3].

In this paper we carry out a direct numerical experiment to investigate temperature dependencies of thermodynamic equilibrium values of “electronic part of total energy” and electronic heat capacity in quasi-one-dimensional molecular chains. The computations have simulated homogeneous adenine–thymine polynucleotide sequences with excess charge carriers moving along adenine chain (polyA).

The knowledge of thermodynamic quantities is essential for understanding many fundamental properties of materials. An important characteristic of all kinds of materials is their heat capacity. For DNA nanobioelectronics, of primary concern is calculation of electronic part of the polynucleotide chains heat capacity. Measurements of temperature dependence of electronic heat capacity give the knowledge of the concentration of current carriers in a molecule, quantum phase transitions, structural properties of materials, etc. In the context of innovative development of high-accuracy calorimetry and nanocalorimetry [4–6] calculation of

temperature dependencies of electronic heat capacities of homogeneous chains is a topical problem.

The model is based on Holstein Hamiltonian for charge transfer along a chain [7–12]:

$$\hat{H} = \sum_{m,n} v_{nm} |m\rangle \langle n| + \sum_n \chi_n u_n |n\rangle \langle n| + \frac{1}{2} \sum_n M \dot{u}_n^2 + \frac{1}{2} \sum_n K u_n^2. \quad (1)$$

Here v_{mn} ($m \neq n$) are matrix elements of the electron transition between m -th and n -th sites (depending on overlapping integrals), v_{nn} is the electron energy on the n -th site, χ_n is a constant of electron coupling with displacements u_n of the n -th site from the equilibrium position, M is the site's effective mass, K is an elastic constant. Choosing the wave function Ψ in the form $\Psi = \sum_{n=1}^N b_n |n\rangle$, where b_n is the amplitude of the probability of charge (electron or hole) occurrence on the n -th site ($n = 1, \dots, N$, N is the chain length), from Hamiltonian (1) for homogeneous chain we get motion equations:

$$i\hbar \dot{b}_n = v_{n,n-1} b_{n-1} + v_{n,n+1} b_{n+1} + \chi u_n b_n, \quad (2)$$

$$\ddot{u}_n = -\omega^2 u_n - \chi |b_n|^2 - \gamma \dot{u}_n + A_n(t). \quad (3)$$

Classical subsystem (3) includes a term with friction (γ is a friction coefficient) and a random force $A_n(t)$ such that $\langle A_n(t) \rangle = 0$, $\langle A_n(t) A_m(t+s) \rangle = 2k_B T \gamma \delta_{nm} \delta(s)$ which simulate a thermostat with a temperature T . Such a way of simulating the thermostat temperature by Langevin equations (3) is well known [13–15].

* Corresponding author.

E-mail address: fialka@impb.psn.ru (N. Fialko).

The model parameters corresponding to nucleotide pairs are [11,16–24,8]: $M = 10^{-21}$ g, terahertz frequency of sites oscillations $\omega = 10^{12}$ s $^{-1}$ corresponds to rigidity of hydrogen bonds $K \approx 0.062$ eV/Å 2 , the coupling constant $\chi = 0.13$ eV/Å. In homogeneous adenine chain the matrix element of the transition between neighbor sites is $\nu_{n,n\pm 1} = -\nu$, $\nu = 0.030$ eV.

For a given temperature, we computed set of samples (trajectories of system (2), (3) from various initial data and with various generated “random” time-series) and calculated the time dependence of the total energy $\langle E_{tot}(t) \rangle$ averaged over samples (where in individual sample $E_{tot}(t) = \langle \Psi | \hat{H} | \Psi \rangle$). Individual trajectories were calculated in two ways: by 2o2s1g-method [25] and with matrix exponential [26] where forced renormalization was added (the total probability of charge’s occurrence in the system must be equal to 1, so variables b_n are “corrected” so that $\sum |b_n(t)|^2 = 1$).

Usually we dealt with two sets, each including 100 samples. The first set is calculated from polaron initial data corresponding to the lowest energy E_{pol} . The second one – from the uniform distribution $|b_n(t=0)|^2 = 1/N$, for which the velocity and displacement of sites were determined from thermodynamic equilibrium distribution for a given temperature. The second variant of the initial data at $T = 0$ corresponds to the highest energy of the system. Calculations were carried out for large time intervals (for more detail, see [27]), until the graphs of time dependencies $\langle E_{tot}(t) \rangle$ obtained for each set of samples became similar. Then the equilibrium value of $\langle E_{tot}(T) \rangle$ was calculated for a given thermostat temperature T .

Having found $\langle E_{tot}(T) \rangle$, we made a numerical estimate of the electronic part of the total energy $E_e = \langle E_{tot}(T) \rangle - Nk_B T$, i.e. we subtracted the heat energy of the N chain oscillators from the total energy of the system. To assess the heat capacity C_V we used two methods so that to check the quality of the calculated ensemble from which the averages were found:

$$C_V = \frac{\partial \langle E_{tot}(T) \rangle}{\partial T} = \frac{1}{k_B T^2} (\langle E_{tot}^2(T) \rangle - \langle E_{tot}(T) \rangle^2).$$

The results obtained by these two procedures are close. The electronic heat capacity C_e was calculated by formulae $C_e = \partial E_e / \partial T = C_V - Nk_B$.

For various thermostat temperatures, we calculated the value of the total energy in thermodynamic equilibrium $\langle E_{tot}(T) \rangle$ for polyA fragments of different lengths. Fig. 1 shows the results obtained for chains of 19, 40 and 60 sites.

Obviously, $\langle E_{tot}(T) \rangle$ depends on the chain length N . The electronic part of the total energy $E_e(T)$ is also different for chains of different lengths. However, the qualitative behavior is similar. Fig. 1a shows the results of calculation of $E_e(T)$. Fig. 1b demonstrates the dependence of the ratio of C_e and heat capacity of the N site chain on chain thermal energy $C_e / (Nk_B)$.

For $T = 0$, $E_e = E_{pol}$, as the temperature grows, $E_e(T)$ increases and a charge passes on from polaron state to a delocalized one. The polaron decay temperature depends not only on the model parameters but also on the chain length [27]: the larger is N , the less is the decay temperature. As the temperature grows still further, E_e becomes a constant, which, judging from calculations, is a function of the chain length N . This constant is inside the conductivity band determined by eigenvalues of W_k for a rigid chain (for $\chi = 0$) [28]: $W_k = -2\nu \cos[k\pi / (N + 1)]$, $k = 1, \dots, N$, and is close to zero, i.e. the midpoint of the conductivity band, Fig. 1a.

Fig. 1b suggests that as the chain length increases, the peak $C_e / (Nk_B)$ becomes higher and more sharp, and shifts in respect of temperature toward zero.

As $T \rightarrow 0$, the normalized electronic heat capacity is independent of the chain length and is close to heat capacity of a classical site k_B (Fig. 1b). Notice that the semiclassical approxima-

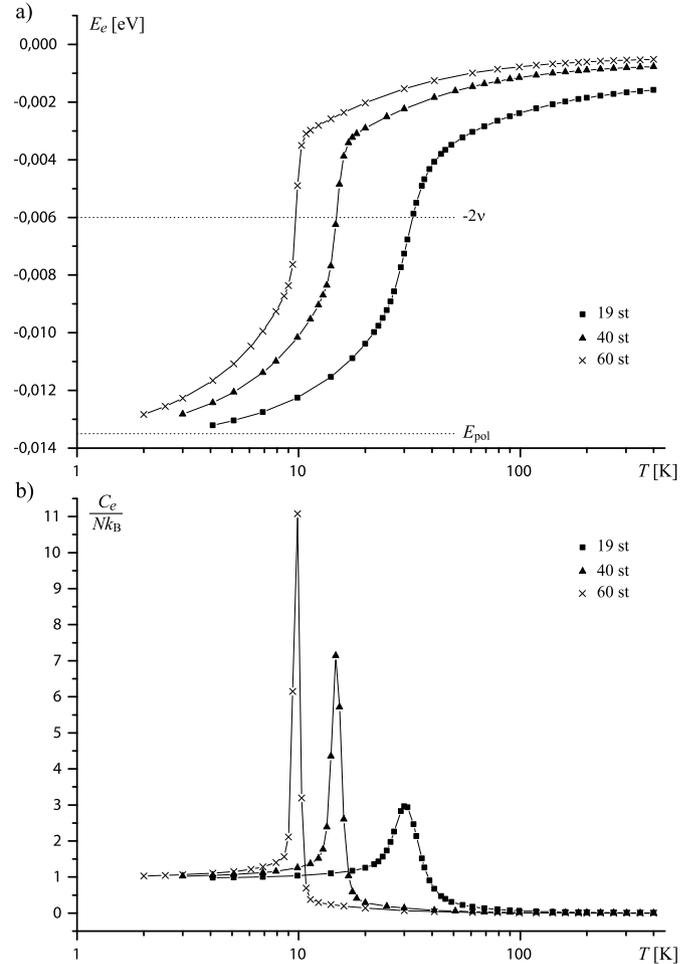


Fig. 1. Results of calculations of thermodynamically equilibrium values. a) Electronic part of the total energy $E_e(T)$ for chains of length 19, 40 and 60 sites. Dashed lines show polaron energies E_{pol} and the lower bound of the conductivity band 2ν . b) Normalized electronic heat capacity.

tion has meaning when the temperature is higher than the Debye one Θ ($k_B \Theta = \hbar \omega$) [15]. For the DNA parameters used in this work $\Theta \approx 8$ K. Hence the peaks of electronic heat capacity for $N \geq 40$ (Fig. 1b) falls in the range of inapplicability of the model under consideration. In short chains ($N < 20$) the electronic heat capacity peaks will be observed at temperatures $T > \Theta$, however they are less pronounced. For $N = 19$, $\max C_e(T) \approx 57k_B \approx 0.0049$ eV/K for $T \approx 30$ K, for shorter chains the peak will be still lower.

If we perform rescaling so that the variable x be not the temperature, but the energy of a classical chain $E_{class} = k_B N T = x$, then as is seen from Fig. 2a, the values of $E_e(x)$ for different N are located in close proximity to one curve. Fig. 2b shows the results of calculation of the normalized electronic heat capacity $y(x) = C_e(x) / Nk_B$. On this scale the heat capacity peaks coincide at abscissa ($x \approx 0.05$) for different N . The decrease of $y(x)$ following the peak is nearly similar in all the cases. We approximated the values obtained by power law $y = Const \cdot x^b$ and found $b \approx -2$, i.e. when a charge in a chain is delocalized the electronic heat capacity of a charge in a chain of N sites decreases approximately as $(NT)^{-2}$.

The peaks of normalized heat capacity at $x_{cr} \approx 0.05$ (Fig. 2b) correspond approximately to the energy value $E_e = -2\nu = -0.06$ eV (bottom of the conductivity band) in Fig. 2a.

In our previous work [27], having calculated the delocalization parameter we showed that a polaron in quasi-one-dimensional

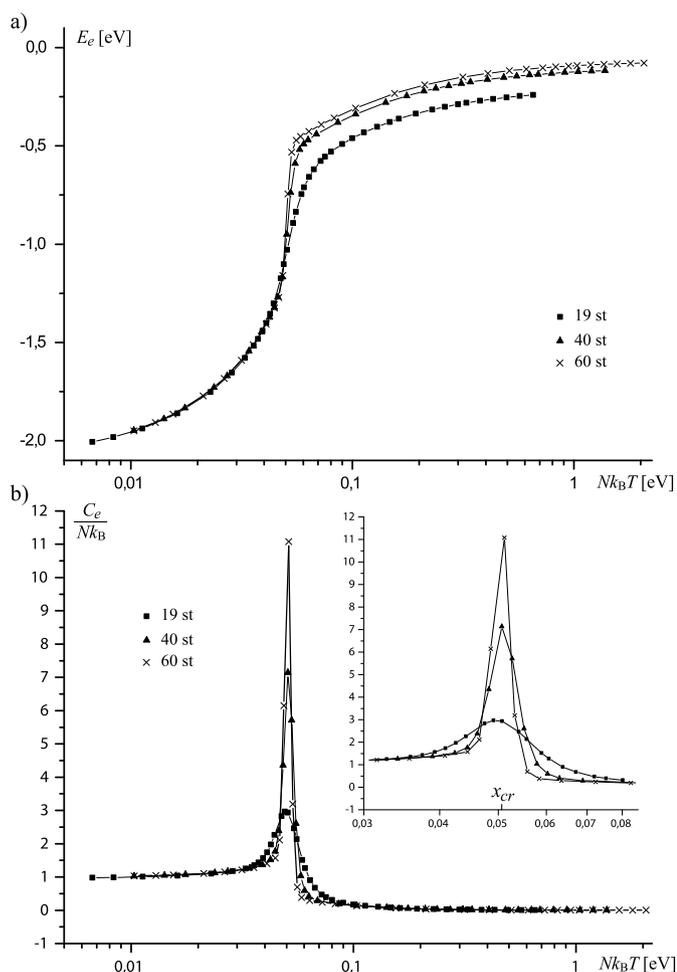


Fig. 2. Rescaled results of calculations. a) Dependence of the charge energy E_e on the energy of a classical chain. b) Dependence of normalized electronic heat capacity C_e/Nk_B on the energy of a classical chain. The inset shows the peak of the function in more detail.

molecular chains has a characteristic decay temperature depending on the chain length. Obviously, this polaron behavior should manifest itself in thermodynamic properties of the electronic part of the DNA heat capacity. The peaks of the temperature dependence of the electronic heat capacity shown in Fig. 2 just fall into the range of polaron decay temperatures. The peak at x_{cr} corresponds to the transition between two different types of state. First is the polaron state with localized charge (Fig. 2b, left from the position of peak x_{cr}). The second type is delocalized state, when the probability density is randomly distributed along the chain (Fig. 2b, right from x_{cr}).

The results of Fig. 2b seem paradoxical at low temperatures, because at $T \rightarrow 0$ the value of the electronic heat capacity C_e is equal to the “macroscopic value” Nk_B if $N \rightarrow \infty$. Actually, the upper bound of the polaron state x_{cr} is a constant energy, i.e. independent of N and T . Thus, the heating energy $Nk_B T$ for transition from polaron state to delocalized one is finite even for infinite chain and is equal to x_{cr} .

Based on the results obtained let us assess the possibility of measuring the electron part of the DNA heat capacity. We will proceed from the fact that the present-day high-accuracy calorimetry enable one to measure the energy difference of about of attojoules ($E = 10^{-18}$ J) [29]. If we assume that the characteristic energy of the polaron state in DNA is $\sim 5 \cdot 10^{-2}$ eV ($\approx 8 \cdot 10^{-21}$ J) and one polaron occurs in a chain of length less than 100 sites, then we get that for the above-mentioned accuracy of measurements, the

number of polynucleotide fragments measured by a calorimeter should be greater than 100. This condition is easily fulfilled for not too strongly diluted DNA solutions. In other words, the temperature dependence of the electronic heat capacity can reasonably be measured experimentally. Bearing in mind fast progress in improving the accuracy of calorimeters it is reasonable to expect that in the near future a new branch, such as DNA nanocalorimetry will emerge.

An important field of application of electronic DNA nanocalorimetry is to use it for measuring the concentration of current carriers in DNA chains playing the role of nanowires. Another essential trend is to use nanocalorimetry for determining nucleotide sequences in mapping on the human genome [30].

In this paper we dealt with homogeneous chains. The existence of a temperature interval of polaron decay is a general property which will take place in inhomogeneous chains too. One would expect that in inhomogeneous DNA sequences there is also a peak of heat capacity. The location and shape of the peak in this case will be highly specific to the location of an electron in a chain which makes possible noninvasive electronic way of mapping on the human genome.

Acknowledgements

The authors are thankful to the Joint Supercomputer Center of RAS for computer resources provided. The work was done with partial support from the Russian Foundation for Basic Research, projects No. 16-07-00305, 14-07-00894, 15-07-06426, and Russian Science Foundation, project 16-11-10163.

References

- [1] V. Lakhno, DNA nanobioelectronics, *Int. J. Quant. Chem.* 108 (11) (2008) 1970–1981.
- [2] A. Offenhäuser, R. Rinaldi (Eds.), *Nanobioelectronics – for Electronics, Biology, and Medicine*, Springer, New York, 2009.
- [3] T. Chakraborty (Ed.), *Charge Migration in DNA. Perspectives from Physics, Chemistry, and Biology*, NanoScience and Technology Series, vol. XVIII, Springer, New York, 2007.
- [4] G. Ithier, E. Collin, P. Joyez, D. Vion, D. Esteve, J. Ankerhold, H. Grabert, Zener enhancement of quantum tunneling in a two-level superconducting circuit, *Phys. Rev. Lett.* 94 (5) (2005) 057004.
- [5] G. Bruylants, J. Wouters, C. Michaux, Differential scanning calorimetry in life science: thermodynamics, stability, molecular recognition and application in drug design, *Curr. Med. Chem.* 12 (17) (2005) 2011–2020.
- [6] H. Esfandyarpour, B. Zheng, R. Pease, R. Davis, Structural optimization for heat detection of DNA thermosequencing platform using finite element analysis, *Biomicrofluidics* 2 (2008) 024102.
- [7] T. Holstein, Studies of polaron motion: part I. The molecular-crystal model, *Ann. Phys.* 8 (1959) 325–342.
- [8] N. Fialko, V. Lakhno, Nonlinear dynamics of excitations in DNA, *Phys. Lett. A* 278 (2000) 108–111.
- [9] S. Alexandre, E. Artacho, J. Soler, H. Chacham, Small polarons in dry DNA, *Phys. Rev. Lett.* 91 (10) (2003) 108105.
- [10] E. Starikov, Electron–phonon coupling in DNA: a systematic study, *Philos. Mag.* 85 (29) (2005) 3435–3462.
- [11] V. Lakhno, Nonlinear models in DNA conductivity, in: E. Starikov, J.P. Lewis, S. Tanaka (Eds.), *Modern Methods for Theoretical Physical Chemistry of Biopolymers*, Elsevier, 2006, pp. 461–481.
- [12] Y. Wang, L. Fu, K.-L. Wang, Extended Holstein small polaron model for charge transfer in dry DNA, *Biophys. Chem.* 119 (2) (2006) 107–114.
- [13] P. Turg, F. Lantelme, H. Friedman, Brownian dynamics: its application to ionic solutions, *J. Chem. Phys.* 66 (7) (1977) 3039–3044.
- [14] E. Helfand, Brownian dynamics study of transitions in a polymer chain of bistable oscillators, *J. Chem. Phys.* 69 (1978) 1010–1018.
- [15] P. Lomdahl, W. Kerr, Do Davydov solitons exist at 300 K?, *Phys. Rev. Lett.* 55 (11) (1985) 1235–1238.
- [16] A. Voityuk, N. Roesch, M. Bixon, J. Jortner, Electronic coupling for charge transfer and transport in DNA, *J. Phys. Chem. B* 104 (2000) 9740–9745.
- [17] J. Jortner, M. Bixon, A. Voityuk, N. Roesch, Superexchange mediated charge hopping in DNA, *J. Phys. Chem. A* 106 (2002) 7599–7606.

- [18] P. Borer, S. Pante, A. Kumar, N. Zunatta, A. Martin, A. Hakkinen, G. Levy, 13C-NMR relaxation in three DNA oligonucleotide duplexes: model-free analysis of internal and overall motion, *Biochemistry* 33 (1994) 2441–2450.
- [19] V. Lisy, P. Miskovsky, P. Schreiber, A simple model of low-frequency vibrations in DNA macromolecules, *J. Biomol. Struct. Dyn.* 13 (4) (1996) 707–716.
- [20] H. Urabe, Y. Sugawara, M. Ataka, A. Rupprecht, Low-frequency Raman spectra of lysozyme crystals and oriented DNA films: dynamics of crystal water, *Biophys. J.* 74 (1998) 1533–1540.
- [21] F. Grozema, Y. Berlin, L. Siebbeles, Sequence-dependent charge transfer in donor–DNA–acceptor systems: a theoretical study, *Int. J. Quant. Chem.* 75 (1999) 1009–1016.
- [22] P. Neill, A. Parker, M. Plumb, L. Siebbeles, Guanine modifications following ionization of DNA occurs predominantly via intra- and not interstrand charge migration: an experimental and theoretical study, *J. Phys. Chem. B* 105 (2001) 5283–5290.
- [23] D. Basko, E. Conwell, Self-trapping versus trapping: application to hole transport in DNA, *Phys. Rev. E* 65 (2002) 061902.
- [24] V. Lakhno, V. Sultanov, B. Pettitt, Combined hopping-superexchange model of a hole transfer in DNA, *Chem. Phys. Lett.* 400 (1–3) (2004) 47–53.
- [25] H. Greenside, E. Helfand, Numerical integration of stochastic differential equations II, *Bell Syst. Tech. J.* 60 (1981) 1927–1940.
- [26] E. Sobolev, D. Tikhonov, N. Fialko, On the numerical solution of the discrete Holstein model, in: Abstracts of XIX All-Russian Conference “Theoretical Foundations and Designing Numerical Algorithms of Problem Solving in Mathematical Physics”, dedicated to the memory of K.I. Babenko, September 10–16, 2012, Keldysh Institute of Applied Mathematics RAS, 2012, p. 90 (in Russian).
- [27] V. Lakhno, N. Fialko, On the dynamics of a polaron in a classical chain with finite temperature, *Zh. Eksp. Teor. Fiz. (JETP)* 120 (2015) 125–131.
- [28] V. Lakhno, V. Sultanov, Band structure of the spectra of Hamiltonians of regular polynucleotide duplexes, *Theor. Math. Phys.* 176 (3) (2013) 1194–1206.
- [29] O. Bourgeois, S. Skipetrov, F. Ong, J. Chaussy, Attojoule calorimetry of mesoscopic superconducting loops, *Phys. Rev. Lett.* 94 (5) (2005) 057007.
- [30] H. Esfandarypour, R. Pease, R. Davis, Picocalorimetric method for DNA sequencing, *J. Vac. Sci. Technol. B* 26 (2) (2008) 661.