
ELECTRONIC PROPERTIES OF SOLID

On the Calculation of Thermodynamic Quantities in the Holstein Model for Homogeneous Polynucleotides

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Abstract—The dynamics of a system for different types of polarons, i.e., in polythymine nucleotides (large-radius polaron), in polyadenine fragments (small-radius polaron), and in polyguanine DNA (intermediate case) at different thermostat temperatures are calculated using the semi-classical Holstein model. The temperature dependences of the thermodynamic equilibrium values of the total energy, the energy of an excess charge, and the electronic heat capacity have been obtained. For all polaron types, the peak of the electronic heat capacity dependence on temperature separates two modes (polaron and delocalized state). The electronic part of the energy is estimated in the high-temperature limit. In all cases, the electron heat capacity at high temperatures decreases in inverse proportion to the square of the temperature.

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1. INTRODUCTION

The mechanisms of charge transfer in biological macromolecules are of interest for biophysics and nanobioelectronics (a new rapidly developing discipline combining the achievements in nanoelectronics and molecular biology) [1–3]. The knowledge of thermodynamic characteristics is important for explaining many fundamental properties of materials. Their heat capacity is an important characteristic of all types of materials. For DNA nanobioelectronics, the calculation of the electronic part of the heat capacity of polynucleotide chains is of considerable interest.

In this study, the temperature dependences of the excess charge energy in thermodynamic equilibrium and the electronic heat capacity in quasi-one-dimensional molecular chains modeling homogeneous nucleotides are studied using a direct numerical experiment. The model is based on the Holstein Hamiltonian of charge transfer along a chain of diatomic sites [4] in the semiclassical approximation; the motion of a charge is described by the Schrödinger equation, and the site oscillations are described by the classical equations of motion. This is a simple model with quadratic potentials for sites, which is widely used for studying DNA [1, 3, 5–8].

The article is organized as follows. In Section 2, we describe the model, a transition to dimensionless equations of motion, and the values of the parameters typical for model DNA. In Section 3, we describe the

methods for calculating the values in thermodynamic equilibrium state and the parameters of the model. In Section 4, we consider the results of simulation for three cases: a small-radius polaron (which corresponds to polyA fragments), an intermediate case (polyG fragments), and a large-radius polaron (polyT chains) at different thermostat temperatures. Since the parameters of homogeneous cytosine and adenine fragments are close, we do not consider the polyC case. The temperature dependences of the electronic part of the energy and the electronic heat capacity are constructed.

This study develops the results obtained in [9]. It is shown that the temperature dependence of the electronic heat capacity has a peak at the temperature depending on the chain length. Upon transition from the temperature to the thermal energy of the chain, the abscissas of these peaks coincide. The results of calculations for polyA fragments were published earlier in [10]: the electronic heat capacity peak was described and the possibility of detecting this effect in DNA nanocalorimetry is considered. The results of the calculations for a small-radius polaron are included in this article in order to obtain a more comprehensive description of the dynamics of polarons of different types in thermodynamic equilibrium. In the last section, the results are discussed. The Appendix contains a substantiation for using parameters that make it possible to reduce the computer time for attaining ther-

modynamic equilibrium in the system and can be used to estimate the electron part of the energy in the limit of infinite temperature.

2. MODEL

A molecular chain can approximately be simulated by a discrete chain consisting of sites (sites are molecules or groups of strongly bound atoms that interact with one another relatively weakly). An excess charge (electron or hole) is introduced into a chain. The propagation of a charge affects the motion of sites; conversely, a displacement of a site changes the probability of a charge being located on it. In the case of DNA, a site is a pair of complementary nucleotides interacting via the formation of hydrogen bonds, which can approximately be simulated as an oscillator.

The model is based on the Holstein Hamiltonian for a discrete chain of sites [4]. Choosing wavefunction Ψ in the form

$$\Psi = \sum_{n=1}^N b_n |n\rangle,$$

where b_n is the probability amplitude of finding a charge (electron or hole) at the n th site ($n = 1, \dots, N$, N being the chain length), we obtain the following expression for the state-averaged Hamiltonian $\langle \Psi | \hat{H} | \Psi \rangle$ of the system:

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle = & \sum_{m,n} v_{nm} b_m b_n^* + \frac{1}{2} \sum_n M \dot{u}_n^2 \\ & + \frac{1}{2} \sum_n K \tilde{u}_n^2 + \sum_n \alpha' \tilde{u}_n b_n b_n^*. \end{aligned} \quad (1)$$

Here, v_{mn} ($m \neq n$) are the matrix elements of an electron transition between the m th and the n th sites; v_{nn} is the energy of a charge on the n th site (we are using the nearest neighbors approximation, i.e., $v_{mn} = 0$ if $m \neq n \pm 1$), α' is the constant of coupling of an electron with displacements $\tilde{u}_n$ of the site from the equilibrium position; M is the effective mass of a site; and K is the elastic constant.

For a homogeneous chain, the equations of motion obtained from Hamiltonian (1) after the transition to dimensionless variables have the form

$$i \frac{db_n}{dt} = \eta (b_{n-1} + b_{n+1}) + \chi u_n b_n, \quad (2)$$

$$\frac{d^2 u_n}{dt^2} = -\omega^2 u_n - \chi |b_n|^2 - \gamma \frac{du_n}{dt} + \xi Z_n(t). \quad (3)$$

The dimensionless coefficients are connected with the dimensional coefficients as follows. The matrix element of the transition between adjacent sites is $\eta = v_{n, n \pm 1} \tau / \hbar$, where τ is the characteristic time and $\tilde{t} = \tau t$. In the simulation, we assume that the charge

can propagate only along a DNA strand without hopping to the complementary strand [11–13]. The frequency of site oscillations is $\omega = \tau \sqrt{K/M}$ and the coupling constant is $\chi = \alpha' \sqrt{\tau^3 / \hbar M}$. For simulating the thermostat, we supplemented Eq. (3) with a term with friction (γ is the friction coefficient) and random force $Z_n(t)$ which is the standard Gaussian quantity with the unit distribution; and $\xi^2 = (2k_B T^* \tau / \hbar) \gamma \mathcal{T} = 2E^* \gamma \mathcal{T}$, with T^* being the characteristic temperature and $\mathcal{T} = \tilde{t} / T^*$. The relation between the dimensional and dimensionless parameters is described in greater detail, for example, in [9] or [14].

The total energy (1) corresponding to the system of dynamic equations (2) and (3) in dimensionless form can be written as

$$\begin{aligned} E_{\text{tot}} = & \eta \sum_n b_n b_{n+1}^* + \frac{1}{2} \sum_n v_n^2 \\ & + \frac{\omega^2}{2} \sum_n u_n^2 + \chi \sum_n u_n b_n b_n^*, \end{aligned} \quad (4)$$

where, $v_n = \dot{u}_n$ is the velocity of the n th site. The model parameters corresponding to nucleotide pairs are chosen as follows [15–18]. The effective mass of a site is $M = 10^{-21}$ g (we assume that the masses of the sites are identical; complementary pairs AT and GC differ by 3%); the characteristic time is $\tau = 10^{-14}$ s; $\omega = 0.01$ (the frequency of site oscillations $\tilde{\omega} = 10^{12}$ s $^{-1}$ corresponds to the rigidity $K \approx 0.062$ eV/Å 2 of hydrogen bonds); and coupling constant $\chi = 0.02$ ($\alpha' = 0.13$ eV/Å). The matrix elements of the transition between sites are $\eta = 0.456$ ($v_{AA} = 0.030$ eV) for adenine fragments, $\eta = 1.276$ ($v_{GG} = 0.084$ eV) for a guanine chain, and $\eta = 2.4$ ($v_{TT} = 0.158$ eV) for polyT. The fourth variant (polyC fragment) was not considered because the matrix elements $\eta = 0.623$ of the transition between cytosines ($v_{CC} = 0.041$ eV) are close to the values of v_{AA} , and the results are similar. The characteristic temperature was chosen as $T^* = 1$ K and the scaling factor $E^* = k_B T^* \tau / \hbar \approx 1.309 \times 10^{-3}$. The relation between the dimensional energy and the dimensionless quantity is as follows: $\tilde{E} = (\hbar / \tau) E \approx E \times 6.482 \times 10^{-3}$ eV.

Disregarding temperature ($\mathcal{T} = 0$), we can state that the charge in a chain forms the lowest energy states (polarons) of different types (Fig. 1).

A small-radius polaron (SRP) is formed in polyA fragments; the maximal probability of finding the charge in the middle site is $|b_n|^2 \approx 0.97$ and the total energy is $E_{\text{tot}} = E_{\text{pol}} \approx -2.10$. The polyT chains correspond to a large-radius polaron (LRP), for which $\max |b_n|^2 \approx 0.22$ and $E_{\text{pol}} \approx -4.94$. An intermediate-radius polaron is formed in polyG chains with $\max |b_n|^2 \approx 0.67$ and $E_{\text{pol}} \approx -2.87$.

It should be noted that not the absolute value of E_{tot} but the distance Δ to the lower boundary of the conduction band determined by the matrix element of the transition is significant for the dynamics of the charge. For an infinite chain, it is the band from -2η to 2η , while for finite chains, the lower boundary $W_N = 2\eta \cos[N\pi/(N+1)]$ [19] for a number of sites $N > 20$ differs from -2η in the third significant digit.

3. COMPUTATIONAL METHODS

At a preset thermostat temperature, we calculated a large number of realizations (the trajectories of system (2) and (3) were calculated from different initial data with different generated random time series). Formula (4) was used for calculating the realization-averaged time dependence of the total energy $\langle E_{\text{tot}}(t) \rangle$ and second moment $\langle E_{\text{tot}}^2(t) \rangle$. The dynamics were calculated over time intervals to the attainment of the equilibrium value $\langle E_{\text{tot}}(\mathcal{T}) \rangle$ for a preset thermostat temperature $\mathcal{T}$ (see [9] for details). Individual realizations were integrated using the 2O2S1G algorithm [20] with artificial normalization (the total probability of finding a charge in a system is $\sum |b_n|^2 = 1$; variables b_n were corrected so that the sum of the squares of their moduli were equal to one).

An additional difficulty in calculating the dynamics of system (2) and (3) was that the characteristic times of quantum (2) and classical (3) subsystems in simulating the charge transfer in the DNA differed by two orders of magnitude. Therefore, it takes a long time to attain thermodynamic equilibrium in the system and even longer as temperature decrease. Using the basic thermodynamic relations, we can show that for a pair of systems (2) and (3) with parameters (η, ω, χ) and $(\eta, C\omega, C\chi)$, where $C = \text{const}$, the values of the total energy in thermodynamic equilibrium must be identical (see Appendix for details). Since we are interested in the processes of attaining the thermodynamic equilibrium state, we assume that $\chi = 1$ and $\omega = 0.5$ for our calculations. In these calculations, we used the simplifying assumption that the values of the parameters are independent of temperature.

Having derived dependences $\langle E_{\text{tot}}(\mathcal{T}) \rangle$ of the values in thermodynamic equilibrium, we subtract the classical energy of a chain of N oscillators from the total energy and obtain the following estimate of the electron part of the total energy:

$$E_e = \langle E_{\text{tot}}(\mathcal{T}) \rangle - E^* N \mathcal{T}. \quad (5)$$

The values of $\langle E_{\text{tot}}(\mathcal{T}) \rangle$ are also used for calculating the heat capacity $C_V = \partial \langle E_{\text{tot}}(\mathcal{T}) \rangle / \partial \mathcal{T}$ of the system and the electronic heat capacity C_e by direct numerical differentiation,

$$C_e = \partial E_e / \partial \mathcal{T} = C_V - E^* N, \quad (6)$$

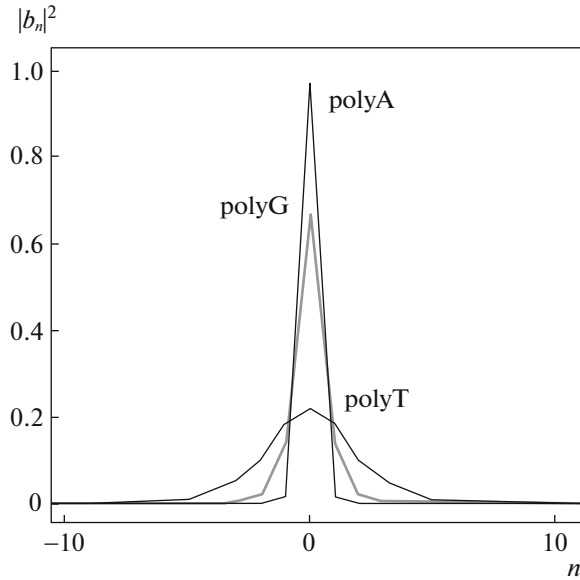


Fig. 1. Probability distribution over sites in the state with the lowest energy $E_{\text{tot}} = E_{\text{pol}}$ for parameters of polyA (SRP), polyT (LRP), and polyG (intermediate-radius polaron) at $\mathcal{T} = 0$.

and using the second moments in the terms of the energy variance by the formula

$$C_{V2} = (\langle E_{\text{tot}}^2(\mathcal{T}) \rangle - \langle E_{\text{tot}}(\mathcal{T}) \rangle^2) / \mathcal{T}^2.$$

For the chosen method of reduction to the dimensionless form, we have $E^* C_V = C_{V2}$. It should be noted that the values of heat capacity calculated using these methods turned out to be close, which indicates that the temperature dependence of heat capacity is qualitatively correct.

4. RESULTS OF COMPUTING EXPERIMENTS

We calculated the values of $\langle E_{\text{tot}}(\mathcal{T}) \rangle$ for three variants of polarons: SRPs (polyA), LRPs (polyT), and intermediate-radius polarons (polyG) at different thermostat temperatures. For each variant, we considered chains of different lengths (20, 40, and 60 sites for SRPs; 40, 60, and 80 sites for the intermediate case; and 40, 60, 80, and 100 sites for LRPs).

4.1. Electron Part of Energy

Obviously, $\langle E_{\text{tot}}(\mathcal{T}) \rangle$ depends on the chain length. The values of the electron part $E_e(\mathcal{T})$ (5) of the total energy for chains of different lengths are also different. However, their qualitative behavior is almost the same ($E_e \approx E_{\text{pol}}$ at $\mathcal{T} = 0$ and increases with temperature because of the transitions from the polaron states to delocalized states). The temperature of polaron

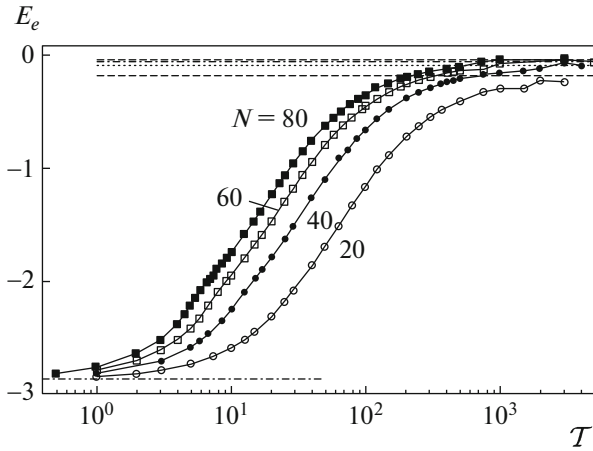


Fig. 2. Temperature dependences of E_e (5) on the semilogarithmic scale for polyG fragments. Dashed lines at the top show the limiting values of (7) for the corresponding values of N ; the polaron energy is shown at the bottom.

breakup depends not only on model parameters but also on the chain length [9]: the larger the value of N , the lower the breakup temperature. Upon a further increase in temperature, E_e attains a constant value close to zero, which also depends on N . Analytic calculations (see Appendix) lead to the following estimate:

$$E_e \rightarrow -\frac{\chi^2}{\omega^2} \frac{1}{N+1} \quad \text{for} \quad \mathcal{T} \rightarrow \infty. \quad (7)$$

The results of the numerical simulation do not contradict this estimate. Figure 2 shows the $E_e(\mathcal{T})$ curves for an intermediate-radius polaron for different lengths N of the chain.

If we perform rescaling (i.e., choose the dimensionless energy of a classical chain rather than the temperature as variable x , $x = E^*N\mathcal{T}$), the values of $E_e(x)$ for different values of N are found to be close to the same curve. Figure 3 shows the $E_e(x)$ curves for an SRP, intermediate-radius polaron, and LRP.

4.2. Electronic Heat Capacity

After rescaling $x = E^*N\mathcal{T}$, the values of electronic heat capacity C_e (6) are also close to the same curve at high temperatures (when the charge is delocalized along the chain). Abscissas x^* of the peaks of the $C_e(x)$ curves plotted in accordance with the results of the calculations for different values of N are close. If we normalize C_e to the chain length, the resultant curves for specific electronic heat capacity for small values of $\mathcal{T}$ are close, while in the transition region from the polaron states to delocalized states, these curves differ in the peak height.

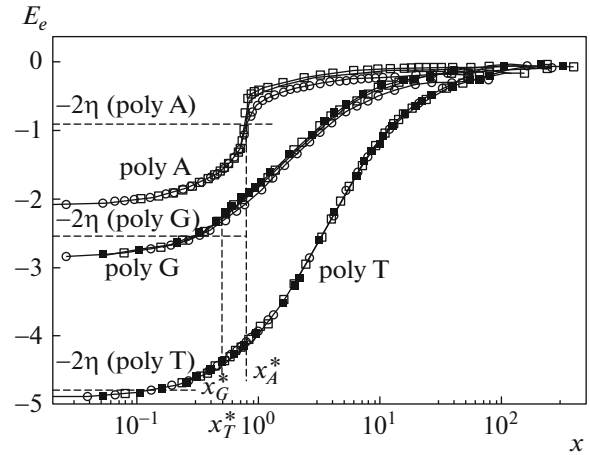


Fig. 3. Dependences of energy E_e of the charge on the energy of a classical chain $x = E^*N\mathcal{T}$. Horizontal dashed lines show the values for the lower boundary of the conduction band in different chains; vertical dashed lines are abscissas x^* corresponding to the peak of the electronic heat capacity. The symbols denoting chains of different lengths N are the same as in Fig. 2, the only exception being that light symbols for polyT fragments denote the results for $N = 100$.

The results of calculations of $C_e(x)/N$ for a SRP, LRP, and intermediate-radius polaron are shown in Fig. 4. It can be seen that for small values of x the values of C_e/N are close to E^* in all three cases. It can also be seen that the peaks for higher values of the chain length N are manifested more clearly. The peaks also depend on the polaron type (for a fixed N , the peak is manifested less strongly for larger polaron radii). We think that the peaks can be put in correspondence with the boundary between two states: the charge is on the average in the polaron state for lower energies and in the delocalized state for higher energies. According to the simulation results, abscissas x^* of the peaks for different polarons are very close: $x^* \approx 0.50$ for polyG and $x^* \approx 0.52$ for polyT.

After passing through the peak, function C_e decreases almost uniformly irrespective of the polaron type (Fig. 5). We approximated the calculated values by the power dependence $C_e = a\mathcal{T}^b$. In all cases, we have $b \approx -2$.

5. DISCUSSION

The peaks of the electronic specific heat on the curves for polyA (Fig. 4a) with abscissa x^* approximately correspond to the energy of the electron part $E_e(x^*) = -2\eta$ of the system in Fig. 3. In other words, for the SRP parameters, the charge passes from the polaron state to the delocalized state in which the energy corresponds to the lower boundary of the conduction band. For polyG (Fig. 4b) and polyT (Fig. 4c), abscissas x^* of the peaks in Fig. 3 correspond

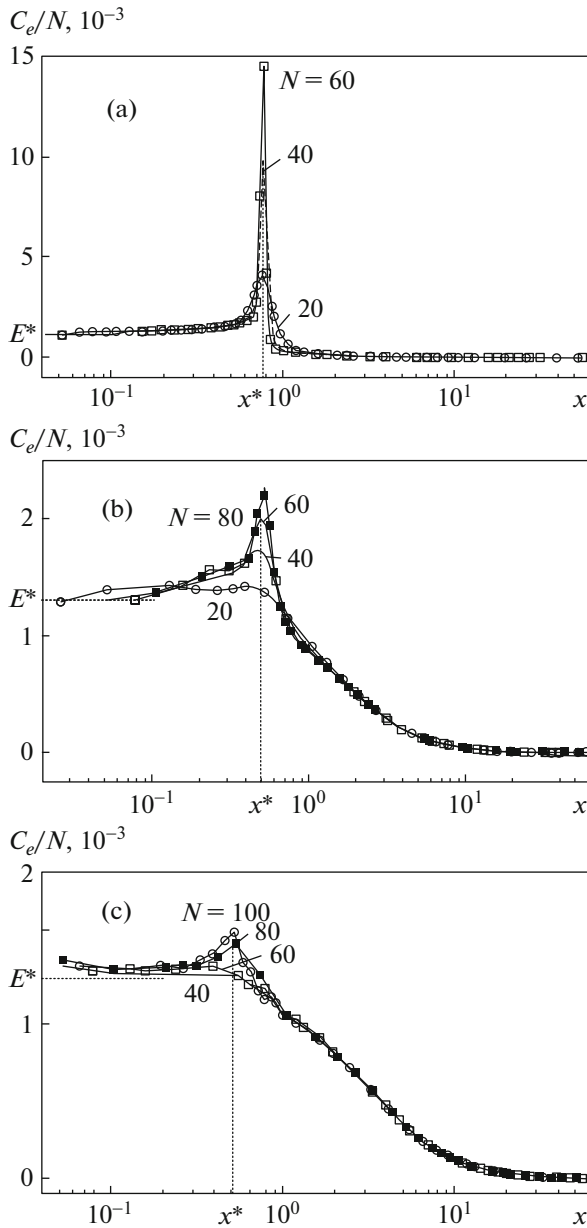


Fig. 4. Specific heat capacity C_e/N as a function of energy $x = E^* N T$ of a classical chain for different polarons: (a) SRP (polyA); (b) intermediate-radius polaron (polyG); and (c) LRP (polyT fragments).

to energies $E_e > -2\eta$. It can be concluded from the calculation results that LRPs are more stable to the action of temperature perturbations than SRPs.

Let us consider the temperature dependences of the electronic heat capacity (Fig. 5). At large values of $\mathcal{T}$ for which the charge is in the delocalized state, the relative dependence

$$\frac{C_e(\mathcal{T})}{C_e(\mathcal{T}_0)} \approx \left(\frac{\mathcal{T}}{\mathcal{T}_0} \right)^{-2}$$

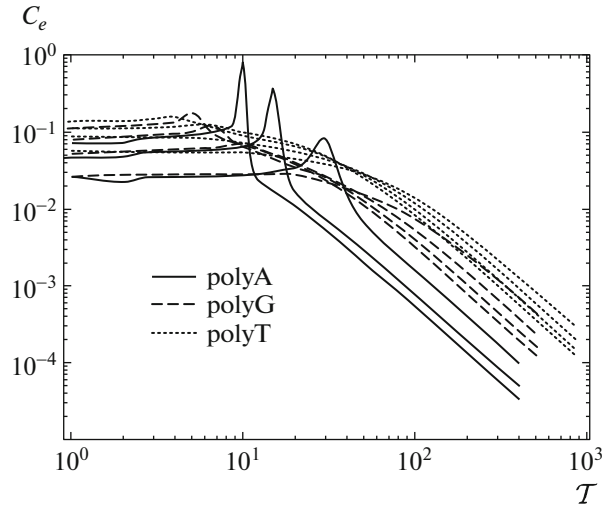


Fig. 5. Temperature dependences of the electronic heat capacity. Chains of the same type are shown by the same curves: the lowermost curves for small values of $\mathcal{T}$ (and upper-lying curves of the same type for large $\mathcal{T}$) correspond to $N = 20$; the next curves correspond to $N = 40, 60$, and 80 ; the uppermost dotted curve corresponds to polyT of length $N = 100$ sites for low values of $\mathcal{T}$. For large $\mathcal{T}$, the same curve is the lowermost of all curves for polyT.

is the same for all values of η according to the calculation results; i.e., the electronic heat capacity in the high-temperature range is mainly determined by the ratio χ/ω (by the properties of the classical subsystem and the coupling constant), and the value of the matrix element η weakly affects C_e .

With an increasing chain length, the C_e peak becomes higher, and its top is shifted towards zero on the temperature scale. The semiclassical approximation is applicable when the temperature is higher than the Debye temperature ($k_B \tilde{T} > \Theta = \hbar \tilde{\omega}$) [21]. For the chosen DNA parameters, we have $\mathcal{T} \approx 8$. It turns out that the C_e peaks for $N \geq 40$ (see Fig. 5) fall into the nonphysical region of the model in question. For a chain length $N < 40$ for LRP and intermediate-radius polaron, the peak on the $C_e(\mathcal{T})$ curve is almost indistinguishable. For polyA with $N < 40$, the C_e peaks are observed at temperatures higher than the Debye temperature, but these peaks are poorly manifested. It should be noted that these results for short chains are also inapplicable. When the chain length is smaller than the polaron radius, the energy and shape of the lowest state may change significantly. For example, the lowest energy of thymine dimer corresponds to a uniform distribution of charge. Such chains are the subjects of special investigations. We believe that the absence of a peak for polyG with $N = 20$ and polyT with chains of length 40 and 60 sites (see Fig. 4) is also due to the insufficient length of the chain although, polarons at $\mathcal{T} = 0$ are localized in the region of approximately 10 sites (see Fig. 1).

The following property of the model is also of interest: for $\mathcal{T} \rightarrow 0$, the electronic specific heat C_e/N is close to constant E^* other than zero (in dimensional quantities, $\tilde{C}_e/N \sim k_B$). The electron part of the heat capacity for temperatures tending to zero is proportional to the chain length. It may appear that in the limit of infinitely long chains and low temperatures, an infinitely high energy is required for heating the charge to a finite temperature. This conclusion seems to be paradoxical because the charge alone cannot lead to a macroscopic action. This paradox is resolved if we put the range of low temperatures in correspondence with the polaron regime. Indeed, when the system is stabilized in a certain state, the charge is acting on the entire chain. In the model under investigation, the line separating the polaron states from delocalized states has the form $N\mathcal{T} = \text{const}$; i.e., the polaron regime exists in all finite-length chains; however, in very long chains, it is limited by ultralow temperatures.

Thus, analyzing the temperature dependences of the heat capacity, we always observe a paradoxical low-temperature asymptotic form; however, in this case, we cannot draw conclusions concerning infinitely long chains. On the other hand, the boundary of the polaron regime has the meaning of energy, but is at the same time a finite constant independent of N and $\mathcal{T}$; i.e., to pass to the branch of the thermalized regime corresponding to high temperatures with a delocalized state of the charge in which the influence of an electron on the chain is weak, we must spend finite energy even for heating an infinitely long chain.

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APPENDIX

Let us consider a system corresponding to the time-independent solution of system (2) and (3) at $\mathcal{T} = 0$ (here, we repeat the well-known procedure [4]):

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

$$0 = -\omega^2 u_n - \chi |b_n|^2 \Rightarrow u_n = -\frac{\chi}{\omega^2} |b_n|^2. \quad (\text{A.2})$$

Substituting expression (A.2) into (A.1) and assuming that $b_n = r_n \exp(iWt)$ and $r_n = \text{const}$, we obtain a system of N cubic equations

$$W r_n = \eta(r_{n-1} + r_{n+1}) - A^2 r_n^3 \quad (\text{A.3})$$

with the condition

$$\sum_{n=1}^N r_n^2 = 1, \quad (\text{A.4})$$

where $A = \chi/\omega$; i.e., the solution of algebraic system (A.3) and (A.4) depends on the ratio A of the coupling constant to the frequency of the classical site. In other words, for $\mathcal{T} = 0$, two systems of ordinary differential equations (2) and (3) with coefficients (η, χ, ω) {I} and $(\eta, C\chi, C\omega)$ {II} have the same steady-state solution $\{r_1, \dots, r_N, W\}$.

The classical steady-state displacements for systems {I} and {II} are different:

$$u_{n\{\text{I}\}} = -\frac{\chi}{\omega^2} r_n^2, \quad u_{n\{\text{II}\}} = -\frac{\chi}{C\omega^2} r_n^2.$$

Substituting these displacements into expression (4) for the total energy and considering that $v_n = 0$, we find that the energies are identical:

$$E_{\text{tot}\{\text{I}\}} = E_{\text{tot}\{\text{II}\}} = \eta \sum_n r_n r_{n\pm 1} - \frac{1}{2} \frac{\chi^2}{\omega^2} \sum_n r_n^4.$$

It should be noted that these arguments are valid for any (not only homogeneous) chain when the ratio $\chi_n/\omega_n = A$ is the same for all sites.

For a finite thermostat temperature $\mathcal{T} \neq 0$ in systems {I} and {II}, the thermodynamic equilibrium values of total energy are also identical. This can be deduced from the basic thermodynamic relations. Let us pass in Hamiltonian (1) to real-valued variables x_n, y_n , where $x_n + iy_n = b_n$, $r_n = |b_n|$. (Formally, $\sqrt{2}x_n$ and $\sqrt{2}y_n$ will be canonically conjugate, but the constants are cancelled out during transformations.)

The partition function in dimensionless form can be written as

$$Z = z^* \int_{\Omega} \exp\left(-\frac{E}{E^* \mathcal{T}}\right) dx_n dy_n du_n dv_n,$$

where z^* is a constant including, in particular, the parameters of transition to the dimensionless system. Expression (4) in these variables has the form

$$E = 2\eta \sum_n (x_n x_{n+1} + y_n y_{n+1}) + \frac{1}{2} \sum_n v_n^2 + \frac{\omega^2}{2} \sum_n u_n^2 + \chi \sum_n u_n (x_n^2 + y_n^2) \quad (\text{A.5})$$

(here and below, we omit the subscript tot). Phase space Ω over which integration is carried out has the form of direct product $\mathbb{R}^{2N} \times S^{2N}$: the boundaries range from $-\infty$ to $+\infty$ for variables u_n and v_n , and variables x_n and y_n satisfy the condition $\sum (x_n^2 + y_n^2) = 1$ (integration over the surface of the sphere). For calculating the total energy $\langle E \rangle$ of the system, we apply the formula for the thermodynamic mean of function F :

$$\langle F \rangle = \int_{\Omega} F \exp\left(-\frac{E}{E^* \mathcal{T}}\right) dx_1 \dots du_N \bigg/ \int_{\Omega} \exp\left(-\frac{E}{E^* \mathcal{T}}\right) dx_1 \dots du_N. \quad (\text{A.6})$$

In expression (A.5), we separate the total squares in the displacements, $(\omega u_n + [\chi/\omega]r_n^2)^2$. Upon substitution of variables $U_n = \omega u_n + [\chi/\omega]r_n^2$, the integration boundaries in expression (A.6) remain unchanged, and the factors in the numerator and denominator are cancelled out. Integrating expression (A.6) with respect to v_n and U_n , we obtain

$$\langle E \rangle = NE^* \mathcal{T}$$

$$\frac{\int_S E_q \exp(-E_q/E^* \mathcal{T}) dx_1 \dots dy_N}{\int_S \exp(-E_q/E^* \mathcal{T}) dx_1 \dots dy_N}, \quad (\text{A.7})$$

where $S = \sum_n (x_n^2 + y_n^2)$ is a sphere in space $\mathbb{R}^{2N}$ and

$$E_q = 2\eta \sum_n (x_n x_{n+1} + y_n y_{n+1}) - \frac{1}{2} \frac{\chi^2}{\omega^2} \sum_n (x_n^2 + y_n^2)^2. \quad (\text{A.8})$$

It can be seen from expressions (A.7) and (A.8) that the values of $\langle E \rangle$ for systems in thermodynamic equilibrium with coefficients (η, χ, ω) and $(\eta, C\chi, C\omega)$ are identical. We performed test calculations for three variants: $\chi = 0.02$, $\omega = 0.01$ (corresponding to the DNA parameters), $\chi = 0.2$, $\omega = 0.1$, and $\chi = 1$, $\omega = 0.5$. The results coincided with the theoretical estimates: after the attainment of thermodynamic equilibrium, the values of E averaged over the realizations are identical.

In estimating the value of quantity (A.7) for high temperatures, we used the simulation results, which showed that the first term in expression (A.8) tends to zero upon an increase in temperature. We assume that for $\mathcal{T} \rightarrow \infty$, term $2\eta \sum_n (x_n x_{n+1} + y_n y_{n+1})$ can be discarded. The denominator in expression (A.7) is transformed into the area of the sphere of unit radius, $2\pi^N/(N-1)!$, and we obtain

$$E_e = \langle E \rangle - NE^* \mathcal{T} \rightarrow \frac{(N-1)!}{2\pi^N} \frac{1}{2\omega^2} \times \sum_{n=1}^N \int_S (x_n^2 + y_n^2)^2 dx_1 \dots dy_N \quad (\text{A.9})$$

here, we have used the commutativity of the sum and integral. The integrand on the right-hand side of expression (A.9) contains the second moments of the

probability of finding the charge at a site. For high temperatures, their values can be assumed to be identical for all sites, i.e.,

$$E_e \approx \frac{1}{2} \frac{\chi^2}{\omega^2} \frac{(N-1)!}{2\pi^N} N \int_S (x_n^2 + y_n^2)^2 dx_1 \dots dx_N. \quad (\text{A.10})$$

The last integral can be evaluated analytically after transition to the spherical coordinates

$$x_1 = \cos \phi_1, \quad y_1 = \sin \phi_1 \cos \phi_2, \dots,$$

$$x_N = \sin \phi_1 \sin \phi_2 \dots \sin \phi_{2N-2} \cos \phi_{2N-1},$$

$$y_N = \sin \phi_1 \sin \phi_2 \dots \sin \phi_{2N-2} \sin \phi_{2N-1},$$

where $\phi_1, \dots, \phi_{2N-2} \in [0, \pi]$ and $\phi_{2N-1} \in [0, 2\pi)$. For the N th site, we obtain

$$\begin{aligned} & \int_S (x_N^2 + y_N^2)^2 dx_1 \dots dx_N \\ &= \int_0^\pi d\phi_1 \int_0^\pi d\phi_2 \dots \int_0^\pi d\phi_{2N-2} \int_0^{2\pi} d\phi_{2N-1} \\ & \quad \times (\sin \phi_1 \dots \sin \phi_{2N-2})^4 \\ & \quad \times \sin^{2N-2} \phi_1 \sin^{2N-3} \phi_2 \dots \sin \phi_{2N-2} \\ &= 2\pi \prod_{n=0}^{2N-2} \int_0^\pi \sin^{2N+3-n} \phi d\phi = 2\pi \frac{\pi^{N-1}}{3 \cdot 4 \cdot 5 \dots N(N+1)}. \end{aligned} \quad (\text{A.11})$$

Here, we have used the recurrent relations for $I_n = \int \sin^n \phi d\phi$: $I_n = I_{n-2}(n-1)/n$ taking into account the integration limits and $I_{2n-1} = 0$. Substituting expression (A.11) into (A.10), we obtain formula (7).

It should be noted that simple arguments lead to the result of the same order of magnitude as expression (7). In the steady-state regime $u_n = -(\chi/\omega^2)|b_n|^2$, the mean value $\langle u_n \rangle$ in thermodynamic equilibrium is the same, and the mean probability of finding a charge at the n th site is $\langle |b_n|^2 \rangle = 1/N$. In expression (4) for energy for $\mathcal{T} \rightarrow \infty$, the first term tends to zero upon averaging, while the sum of the second and third terms tends to energy $E^* N \mathcal{T}$ of the N oscillators plus $(\chi^2/\omega^2)(1/N)$ because $\langle u_n \rangle \neq 0$ and the variance of u_n remains unchanged. The last term in expression (4) after the substitution of the mean value of u_n gives

$$E_{\text{int}} = \left\langle \chi \sum_n u_n |b_n|^2 \right\rangle = -\frac{\chi^2}{\omega^2} \sum_n \langle |b_n|^4 \rangle.$$

It follows from the calculation results of [9] that delocalization parameter $\langle R \rangle = 1/\langle \sum |b_n|^4 \rangle \sim N/2$, and we obtain the estimate $E_{\text{int}} \sim -(\chi^2/\omega^2)(2/N)$; i.e., energy $E_e \sim (\chi/\omega)^2(1/N)$.

The difference from expression (7) appears because of the inaccuracy of the estimate of $\langle R \rangle$ [9]. Indeed, using expression (A.11), we obtain $\langle |b_n|^4 \rangle = 2/[N(N+1)]$ and $\langle R \rangle = (N+1)/2$.

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