

Solitary excitations in deoxyribonucleic acid (DNA) double helices

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Dynamical features of solitary excitations in deoxyribonucleic acid (DNA) double helices are described by a revised theory in which the H-bonding energy between complementary base pairs has a more reasonable form. Four modes of sine-Gordon solitons which predict the existence of the open states in DNA double helices are found. By using the statistical-mechanical formalism which has been established previously, the average soliton number density in DNA double helices is estimated as a function of temperature and compared with the experimental results.

I. INTRODUCTION

Recently the existence of an open state in deoxyribonucleic acid (DNA) and synthetic polynucleotide double helices has been demonstrated by hydrogen-deuterium exchange measurements.¹⁻³ Assuming a mobile open unit⁴ diffusing along the double helix, Englander *et al.*⁵ suggested that the open state in DNA may be described as a solitary excitation. Previously, we proposed a soliton theory⁶ in order to give a theoretical explanation of the open states in DNA duplexes. Since our theory had a defect in the expression of H-bonding energy between complementary base pairs, we present here a revised analysis in which the H-bonding energy has a more general and reasonable form. We also adopt here the same simplified model as in the previous paper that each nucleotide base can rotate around an axis parallel to the helical axis of the duplex, accompanying a rotation of the sugar and the phosphate of the nucleotide to which the base belongs.

In Sec. II we formulate our Hamiltonian which gives three types of sine-Gordon equations. Corresponding to the different solvent conditions, four modes of solitary excitations are found. In Sec. III the average soliton number density of our system is given by the use of earlier results⁷⁻¹¹ on the statistical mechanics of nonlinear fields, assuming that the uncoupled 2π solitons only are excited in the solvent condition under which the H-D exchange measurements¹⁻³ was performed.

II. HAMILTONIAN AND SOLITON SOLUTIONS

The B form of DNA and polynucleotide double helices is schematically represented in Fig. 1(a), where each arrow shows the direction of the base attached to the strand, and the conjugated base pairs are indicated by the pairs of arrows arranged in horizontal parallel planes separated by a distance of $a = 3.4 \text{ \AA}$. The z axis is a tenfold screw axis. Figure 1(b) shows a projection of the n th complementary base pair on the x - y plane, where B_n denotes the n th base belonging to one of the two strands and B'_n denotes the complementary base belonging to the other strand, and these form an H-bonded base pair in an ordered state. The directions of B_n and B'_n in the horizontal plane are specified by the rotational angles of the directional vectors $P_n B_n$ and $P'_n B'_n$ of the bases around the axes P_n and P'_n , respectively, which are denoted by

$$\chi_n = \angle P'_n P_n B_n, \quad \chi'_n = \angle P_n P'_n B'_n, \quad (2.1)$$

where the rotational axes of n th and n' th nucleotides, P_n and P'_n , respectively, are parallel to the z axis. The conformation and stability of DNA and polynucleotide double helices are mainly determined by the energy of H bonds between interstrand complementary base pairs and the stacking energy between intrastrand adjacent bases and the torsional energy of polynucleotide strands.

Considering that the H-bonding energy between the n th base pair $V_n(\chi_n, \chi'_n)$ is a periodic function of the rotational angles χ_n and χ'_n with the periods 2π , and assuming that $V_n(\chi_n, \chi'_n)$ is an even function with respect to χ_n and χ'_n , we expand $V_n(\chi_n, \chi'_n)$ in the form of a double Fourier series,

$$V_n(\chi_n, \chi'_n) = \sum_{p,q=0}^{\infty} B_{pq}^{nn'} \cos(p\chi_n) \cos(q\chi'_n), \quad (2.2)$$

and approximate it by the first four terms:

$$B_{00}^{nn'} + B_{10}^{nn'} \cos\chi_n + B_{01}^{nn'} \cos\chi'_n + B_{11}^{nn'} \cos\chi_n \cos\chi'_n. \quad (2.3)$$

Adopting mean parameter values for double and triple

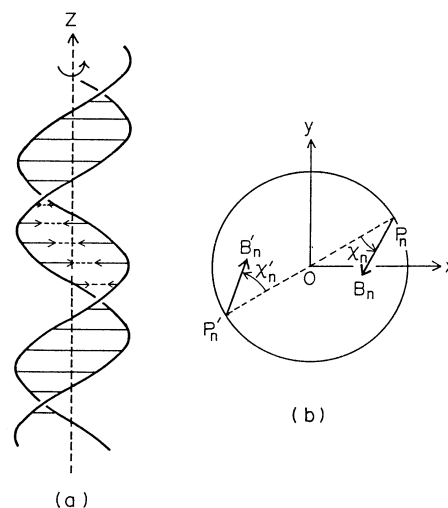


FIG. 1. (a) Schematic representation of the Watson-Crick model, (b) horizontal projections of the complementary base pairs.

H-bonds in the A-T (adenine-thymine) and G-C (guanine-cytosine) base pair $\bar{B}_{pq}^{nn'} = B_{pq}$, considering the symmetry relations $B_{01} = B_{10}$, and taking the B form ($\chi_n = \chi'_n = 0$) as the zero level of energy, the total energy of H-bonds between complementary base pairs can be represented by the following form without losing generality:

$$\sum_n [A(1 - \cos\chi_n) + A(1 - \cos\chi'_n) + B(1 - \cos\chi_n \cos\chi'_n)], \quad (2.4)$$

where A and B are the constants.

By assuming that the stacking energy between intra-strand adjacent bases and the torsional energy of the nucleotide strand are both functions of the relative torsional angles between adjacent bases and that these energies are given in the same functional form, the sum of the stacking and torsional energies may be written as

$$\sum_n \{S[1 - \cos(\chi_n - \chi_{n-1})] + S[1 - \cos(\chi'_n - \chi'_{n-1})]\}, \quad (2.5)$$

where S is the constant, and here the B form is taken as the zero level of the energy. The H-bonding energy and

the sum of the stacking and torsional energies associated with the n th base are obtained by setting $\chi_n = \pi$ and fixing all other χ_m ($m \neq n$) and χ'_n at zero in Eqs. (2.4) and (2.5); these are represented by $2(A + B)$ and $4S$, respectively. Then the Hamiltonian of DNA and synthetic polynucleotide double helices can be written as

$$\begin{aligned} \mathcal{H} = \sum_n \{ & \frac{1}{2}I(\dot{\chi}_n^2 + \dot{\chi}'_n{}^2) + A(1 - \cos\chi_n) \\ & + A(1 - \cos\chi'_n) + B(1 - \cos\chi_n \cos\chi'_n) \\ & + S[1 - \cos(\chi_n - \chi_{n-1})] \\ & + S[1 - \cos(\chi'_n - \chi'_{n-1})]\}, \end{aligned} \quad (2.6)$$

where the first term represents the kinetic energy of the rotational motion of the n th nucleotide base accompanied by the n th nucleotide sugar and phosphate around the axis P_n , in which I is the mean value of the moment of inertia of the nucleotide around axis P_n .

Introducing the fields of rotational angles in the continuum approximation,

$$\chi_n(t) \rightarrow \chi(z, t), \quad \chi'_n(t) \rightarrow \chi'(z, t), \quad (2.7)$$

our Hamiltonian can be written alternatively as follows:

$$\mathcal{H} = \int \frac{dz}{a} [\frac{1}{2}I(\dot{\chi}^2 + \dot{\chi}'^2) + A(1 - \cos\chi) + A(1 - \cos\chi') + B(1 - \cos\chi \cos\chi') + \frac{1}{2}Sa^2(\chi_z^2 + \chi'_z{}^2)] \quad (2.8)$$

$$= \int \frac{dz}{a} \left[\frac{1}{2}I(\dot{\psi}^2 + \dot{\phi}^2) + 2A \left[1 - \cos\frac{\psi}{2} \cos\frac{\phi}{2} \right] + B \left[1 - \frac{1}{2}(\cos\psi + \cos\phi) \right] + \frac{1}{4}Sa^2(\psi_z^2 + \phi_z^2) \right], \quad (2.9)$$

where

$$\psi = \chi + \chi', \quad \phi = \chi - \chi', \quad (2.10)$$

and χ_z, ψ_z , etc. denote $\partial\chi/\partial z, \partial\psi/\partial z$, etc. From the Lagrangians corresponding to Eqs. (2.8) and (2.9), we obtain the following Euler-Lagrange equations, respectively:

$$I\ddot{\chi} + A \sin\chi + B \sin\chi \cos\chi' - Sa^2\chi_{zz} = 0, \quad (2.11a)$$

$$I\ddot{\chi}' + A \sin\chi' + B \sin\chi' \cos\chi - Sa^2\chi'_{zz} = 0, \quad (2.11b)$$

$$I\ddot{\psi} + 2A \sin\frac{\psi}{2} \cos\frac{\phi}{2} + B \sin\psi - Sa^2\psi_{zz} = 0, \quad (2.12a)$$

$$I\ddot{\phi} + 2A \sin\frac{\phi}{2} \cos\frac{\psi}{2} + B \sin\phi - Sa^2\phi_{zz} = 0, \quad (2.12b)$$

where $\ddot{\chi}, \chi_{zz}$, etc. denote $\partial^2\chi/\partial t^2, \partial^2\chi/\partial z^2$, etc. Assuming that, by taking an adequate acidity and salt concentration, we can realize a solvent condition $A \simeq 0$ in which the H-bonding energy between the base pair is almost equal to that between the bases and water molecules of the solvent, we study the dynamics of our system including the case $A = 0$.

A. The case $A = 0$

Since the constant solutions which satisfy $\sin\chi = 0$ and $\sin\chi' = 0$ are the solutions of Eqs. (2.11a) and (2.11b),

respectively, we obtain the following six sets of solutions of Eqs. (2.11). Two of these correspond to the ground-state solutions,

$$\chi = 2n\pi, \quad \chi' = 2m\pi, \quad (2.13a)$$

$$\chi = (2n + 1)\pi, \quad \chi' = (2m + 1)\pi; \quad (2.13b)$$

others are the uncoupled 2π soliton solutions where the motions of χ and χ' are not coupled,

$$\chi = \phi_s(\xi - \xi_0), \quad \chi' = 2m\pi, \quad (2.14a)$$

$$\chi = 2n\pi, \quad \chi' = \phi_s(\xi - \xi_0), \quad (2.14b)$$

$$\chi = \phi_s(\xi - \xi_0) + \pi, \quad \chi' = (2m + 1)\pi, \quad (2.14c)$$

$$\chi = (2n + 1)\pi, \quad \chi' = \phi_s(\xi - \xi_0) + \pi, \quad (2.14d)$$

where n and m are integers and $\phi_s(\xi - \xi_0)$ is the soliton solution of the following sine-Gordon equation:

$$I\ddot{\chi} + B \sin\chi - Sa^2\chi_{zz} = 0, \quad (2.15)$$

$$\chi = \phi_s(\xi - \xi_0) = 4 \tan^{-1} e^{\pm(\gamma/l)(\xi - \xi_0)}, \quad (2.16)$$

where

$$\begin{aligned} \xi = z - vt, \quad l = (S/B)^{1/2}a, \quad \gamma = (1 - v^2/v_0^2)^{-1/2}, \\ v_0 = (S/I)^{1/2}a, \quad v < v_0. \end{aligned} \quad (2.17)$$

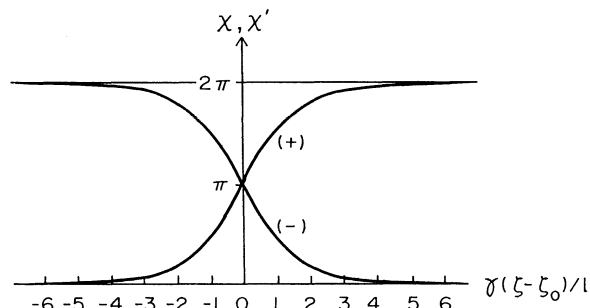


FIG. 2. Kink and antikink soliton solutions of Eqs. (2.15) and (2.23).

The numerical results of Eq. (2.16) are shown in Fig. 2.

On the other hand, Eqs. (2.12a) and (2.12b) are satisfied by the constant solutions $\psi = n\pi$ and $\phi = m\pi$, respectively, and by the soliton solutions $\psi = \phi_s(\xi - \xi_0)$ and $\phi = \phi_s(\xi - \xi'_0)$, respectively. Then Eqs. (2.12) are satisfied by the following sets of solutions:

$$\{\psi = n\pi, \phi = m\pi\}, \quad (2.18a)$$

$$\{\psi = \phi_s(\xi - \xi_0), \phi = m\pi\} \quad (2.18b)$$

$$\{\psi = n\pi, \phi = \phi_s(\xi - \xi'_0)\}, \quad (2.18c)$$

$$\{\psi = \phi_s(\xi - \xi_0), \phi = \phi_s(\xi - \xi'_0)\}. \quad (2.18d)$$

Equation (2.18a) gives the ground-state solutions corresponding to Eqs. (2.13a) and (2.13b), and Eqs. (2.18b) and (2.18c) give the in-phase and out-of-phase coupled π soliton solutions, respectively, where the motions of χ and χ' are coupled:

$$\chi = m'\pi + \frac{1}{2}\phi_s(\xi - \xi_0), \quad \chi' = -m'\pi + \frac{1}{2}\phi_s(\xi - \xi_0), \quad (2.19a)$$

$$\chi = n'\pi + \frac{1}{2}\phi_s(\xi - \xi'_0), \quad \chi' = n'\pi - \frac{1}{2}\phi_s(\xi - \xi'_0). \quad (2.19b)$$

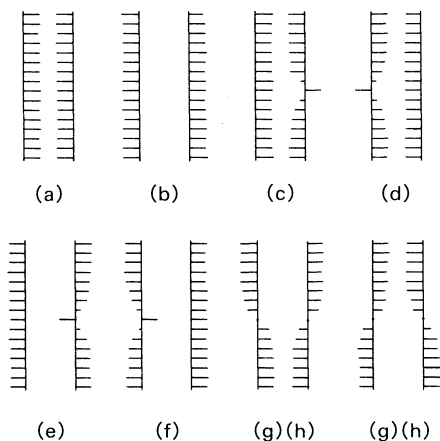


FIG. 3. Ground states and solitary excitations in the case $A=0$ are schematically shown. (a) Eq. (2.13a); (b) Eq. (2.13b); (c) Eq. (2.14a); (d) Eq. (2.14b); (e) Eq. (2.14c); (f) Eq. (2.14d); (g) Eq. (2.19a); (h) Eq. (2.19b).

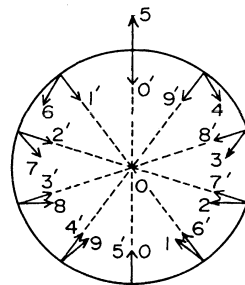


FIG. 4. Horizontal projections of the directions of the bases in uncoupled $2\pi\chi$ solitons which are obtained by setting $\gamma=1$, $l=a$ in Eq. (2.16).

Here the cases m odd, n odd are excluded because they give unstable solutions; then we set $m = 2m'$, $n = 2n'$.

Equation (2.18d) gives two coupled π soliton solutions:

$$\chi = \frac{1}{2}\phi_s(\xi - \xi_0) + \frac{1}{2}\phi_s(\xi - \xi'_0), \quad (2.20)$$

$$\chi' = \frac{1}{2}\phi_s(\xi - \xi_0) - \frac{1}{2}\phi_s(\xi - \xi'_0).$$

These ground state and soliton solutions (2.13a), (2.13b), (2.14a)–(2.14d), (2.19a), and (2.19b), are shown schematically in Figs. 3(a)–3(h), respectively, where in order to show only the rotations of the bases, the double strands of polynucleotide duplex are shown by the two vertical parallel lines, neglecting the screw symmetry of the strands, and the projections of the directional vectors $\overline{P_n B_n}$ of the bases B_n on the lines $P_n P'_n$ are shown by the short horizontal bars. We can easily see by the figures that the lengths of these open configurations in the regions of solitary excitations are about $5a$ – $10a$. The result of numerical calculation of the rotational angles χ_n and χ'_n in the region of solitary excitation is shown in Fig. 4 for case (c) in Fig. 3 in a horizontal projection, where the numbers $0, 1, 2, \dots$ and $0', 1', 2', \dots$ denote the bases belonging to the complementary strands, respectively.

We wish to propose here the role which may be played by a soliton in DNA. It may be supposed that if the condition $A \approx 0$ may be effectively realized by changing the acidity and salt concentration of the solvent adequately, then the coupled π soliton is the solitary excitation with the lowest energy. As seen in Figs. 3(g) and 3(h), this soliton is very interesting physiologically, because a closing or an opening of the structure of DNA can easily be realized by motion of this soliton. Thus a movement of a coupled π soliton only is sufficient for an opening of the structure of DNA in the duplication of DNA and the transcription of mRNA (messenger ribonucleic acid); there is no need to consider such an unlikely motion as a continuous rewinding of the double strands of DNA, which has been supposed so far.

B. The case $A \neq 0$

Since Eqs. (2.11a) and (2.11b) are satisfied by the constant solutions $\chi = n\pi$ and $\chi' = m\pi$, respectively, we obtain sets of solutions of Eqs. (2.11) similar to those of the case $A=0$. But, in this case, odd numbers of n and m correspond to unstable solutions. We therefore obtain the

following three sets of solutions of Eqs. (2.11). One corresponds to the ground states:

$$\chi = 2n\pi, \quad \chi' = 2m\pi, \quad (2.21)$$

and the others are the uncoupled 2π soliton solutions,

$$\chi = \tilde{\phi}_s(\zeta - \zeta_0), \quad \chi' = 2m\pi, \quad (2.22a)$$

$$\chi = 2n\pi, \quad \chi' = \tilde{\phi}_s(\zeta - \zeta_0), \quad (2.22b)$$

where n and m are integers and $\tilde{\phi}_s(\zeta - \zeta_0)$ is a solution of the sine-Gordon equations,

$$I\ddot{\chi} + (A + B)\sin\chi - Sa^2\chi_{zz} = 0, \quad (2.23)$$

$$\chi = \tilde{\phi}_s(\zeta - \zeta_0) = 4 \tan^{-1} e^{\pm(\gamma/\tilde{l})(\zeta - \zeta_0)}, \quad (2.24)$$

where

$$\tilde{l} = [S/(A + B)]^{1/2} a, \quad v < v_0. \quad (2.25)$$

The $\tilde{\phi}_s$ -versus- ζ/\tilde{l} curve, which is obtained from Eq. (2.24), is similar to the ϕ_s -versus- ζ/l curve which is shown in Fig. 2.

On the other hand, Eqs. (2.12a) and (2.12b) are satisfied by the constant solutions $\psi/2 = n\pi$ and $\phi/2 = m\pi$, respectively. Then the solutions of Eqs. (2.12) can be obtained from the following sets of equations:

$$\{\psi = 2n\pi, \phi = 2m\pi\}, \quad (2.26a)$$

$$\{\text{Eq. (2.12a)}, \phi = 2m\pi\}, \quad (2.26b)$$

$$\{\psi = 2n\pi, \text{Eq. (2.12b)}\}. \quad (2.26c)$$

$$\frac{[1 - K \sin^2(\chi/2)]^{1/2} - [\cos^2(\chi/2)]^{1/2}}{\sqrt{1 - K} \sin(\chi/2)} = \begin{cases} e^{\pm(\gamma/\tilde{l})(\zeta - \zeta_0)}, & 0 < \chi < \pi \\ e^{\mp(\gamma/\tilde{l})(\zeta - \zeta_0)}, & \pi < \chi < 2\pi \end{cases} \quad (2.32)$$

where

$$K = B/(A + B), \quad v < v_0 \quad (2.33)$$

with the \pm corresponding to the kink and antikink solutions.

The result of the numerical calculation of Eq. (2.32) for the case $A = B$ ($K = 1/2$) is shown in Fig. 5. The $\tilde{\phi}_s$ -versus- ζ/\tilde{l} curve is quite similar to the ϕ_s -versus- ζ/l (or

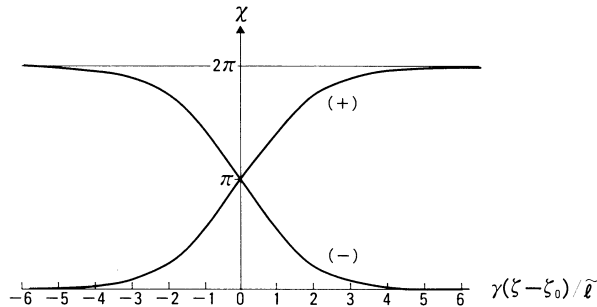


FIG. 5. Kink and antikink soliton solutions of Eq. (2.32).

Equation (2.26a) gives the ground-state solution $\chi = (n + m)\pi$, $\chi' = (n - m)\pi$, when $n + m$ is even and an unstable solution when $n + m$ is odd. Equation (2.26b) gives the relations $\chi - \chi' = 2m\pi$, $\psi = \chi + \chi' = 2\chi - 2m\pi$; then Eq. (2.12a) becomes an extended sine-Gordon equation:

$$I\ddot{\chi} + A \sin\chi + \frac{B}{2} \sin 2\chi - Sa^2\chi_{zz} = 0. \quad (2.27)$$

The constant solution $\chi = n\pi$ of this equation gives the ground-state solution and unstable constant solution combining with $\chi - \chi' = 2m\pi$. In order to get a soliton solution we have rewritten Eq. (2.27) as

$$\ddot{\chi} = v_0^2 \chi_{zz} - \bar{\omega}_0^2 dV/d\chi, \quad (2.28)$$

where

$$\bar{\omega}_0 = (A/I)^{1/2}, \quad V(\chi) = (1 - \cos\chi) + \frac{B}{4A}(1 - \cos 2\chi). \quad (2.29)$$

With the boundary conditions $d\chi/d\zeta = 0$, $\chi = 0$ at $\zeta = \pm\infty$, the first integral is obtained as

$$d\chi/d\zeta = \pm\sqrt{2} \frac{\gamma}{\tilde{l}} [V(\chi)]^{1/2}, \quad (2.30)$$

where

$$\tilde{l} = v_0/\bar{\omega}_0. \quad (2.31)$$

This is integrated to yield the soliton solution $\chi = \tilde{\phi}_s(\zeta - \zeta_0)$ which is given by the equation

$\tilde{\phi}_s$ -versus- ζ/\tilde{l}) curve in Fig. 2. Thus Eq. (2.26b) gives the ground-state solution and in-phase coupled 2π soliton solution

$$\chi = \chi' + 2m\pi = \tilde{\phi}_s(\zeta - \zeta_0). \quad (2.34)$$

Similarly, Eq. (2.26c) gives the ground-state solution and out-of-phase coupled 2π soliton solution

$$\chi = -\chi' + 2n\pi = \tilde{\phi}_s(\zeta - \zeta_0). \quad (2.35)$$

These solutions, (2.21), (2.22a), (2.22b), (2.34), and (2.35), are shown schematically in Figs. 6(a)–6(e), respectively,

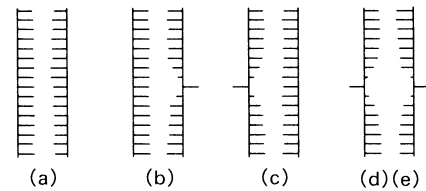


FIG. 6. Ground state and soliton solutions in the case $A \neq 0$ are schematically shown. (a) Eq. (2.21); (b) Eq. (2.22a); (c) Eq. (2.22b); (d) Eq. (2.34); (e) Eq. (2.35).

and these figures also show that the lengths of open configurations are about $5a-10a$.

The energies associated with the four modes of solitons which we found can be calculated by using Eq. (2.8) and the first integrals of Eqs. (2.15), (2.23), and (2.27), respectively, which correspond to Eq. (2.30). We distinguish the case $A=0$ from the case $A \neq 0$, the case of the uncoupled from that of the coupled, and the case of the π soliton from that of the 2π soliton by the indices $A=0$, $A \neq 0$, u , c , π , and 2π , respectively:

$$\begin{aligned}
 E_{u,2\pi}^{A=0} &= \int \frac{dz}{a} \left[\frac{1}{2} I \dot{\phi}_s^2 + B(1 - \cos \phi_s) + \frac{1}{2} S a^2 \phi_{s,z}^2 \right] \\
 &= 8\sqrt{BS} \gamma, \\
 E_{c,\pi}^{A=0} &= \int \frac{dz}{a} \left[\frac{1}{4} I \dot{\phi}_s^2 + \frac{B}{2}(1 - \cos \phi_s) + \frac{1}{4} S a^2 \phi_{s,z}^2 \right] \\
 &= 4\sqrt{BS} \gamma, \\
 E_{u,2\pi}^{A \neq 0} &= \int \frac{dz}{a} \left[\frac{1}{2} I \dot{\bar{\phi}}_s^2 + (A+B)(1 - \cos \bar{\phi}_s) + \frac{1}{2} S a^2 \bar{\phi}_{s,z}^2 \right] \\
 &= 8\sqrt{(A+B)S} \gamma, \\
 E_{c,2\pi}^{A \neq 0} &= \int \frac{dz}{a} \left[I \dot{\bar{\phi}}_s + 2A(1 - \cos \bar{\phi}_s) \right. \\
 &\quad \left. + \frac{B}{2}(1 - \cos^2 \bar{\phi}_s) + S a^2 \bar{\phi}_{s,z}^2 \right] \\
 &= 16\sqrt{AS} f(\xi) \gamma,
 \end{aligned} \tag{2.36}$$

where

$$f(\xi) = \frac{1}{2} \left[\sqrt{1+\xi} + \frac{1}{\sqrt{\xi}} \ln(\sqrt{\xi} + \sqrt{\xi+1}) \right], \quad \xi = B/A. \tag{2.37}$$

Figure 7 shows that the ratio

$$\eta = E_{c,2\pi}^{A \neq 0} / E_{u,2\pi}^{A \neq 0} = 2f(\xi)(1+\xi)^{-1/2} \tag{2.38}$$

approaches 1 with the increase of ξ , that is, $E_{u,2\pi}^{A \neq 0}$ and $E_{c,2\pi}^{A \neq 0}$ coincide with $E_{u,2\pi}^{A=0}$ as $\xi \rightarrow \infty$.

Generally, the energy associated with a single soliton with velocity v is given by the following form:

$$E_s^{(v)} = E_s^{(0)} \gamma = (E_s^{(0)^2} + p_s^2 v_0^2)^{1/2}, \tag{2.39}$$

where p_s is the relativistic momentum and $E_s^{(0)}$ is the rest energy of the soliton,

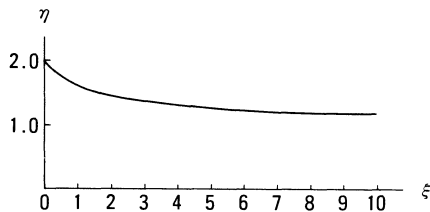


FIG. 7. ξ dependence of η .

$$p_s = M_s^{(0)} v \gamma, \quad E_s^{(0)} = M_s^{(0)} v_0^2. \tag{2.40}$$

Then the rest masses of the four modes of solitons are given by Eqs. (2.36) and (2.40) as follows:

$$\begin{aligned}
 M_{u,2\pi}^{A=0(0)} &= 8(B/S)^{1/2}(R/a)^2 M, \\
 M_{c,\pi}^{A=0(0)} &= 4(B/S)^{1/2}(R/a)^2 M, \\
 M_{u,2\pi}^{A \neq 0(0)} &= 8[(A+B)/S]^{1/2}(R/a)^2 M, \\
 M_{c,2\pi}^{A \neq 0(0)} &= 16(A/S)^{1/2} \phi(\xi)(R/a)^2 M,
 \end{aligned} \tag{2.41}$$

where M and R denote mean mass and mean radius of gyration per nucleotide.

Here we mention that the phonon modes which correlate to the four modes of solitons can be obtained assuming χ is small in Eq. (2.15) for the case $A=0$ and in Eqs. (2.23) and (2.27) for the case $A \neq 0$. We obtain harmonic solutions:

$$\chi \propto \exp[i(kz - \omega t)] = \exp[ik(z - vt)], \tag{2.42}$$

$$\chi' \propto \exp[i(kz - \omega t)] = \exp[ik(z - vt)].$$

For the case $A=0$, k is given by

$$k^2 = (v^2/v_0^2 - 1)^{-1}/l^2, \tag{2.43}$$

and for the case $A \neq 0$

$$k^2 = (v^2/v_0^2 - 1)^{-1}/\tilde{l}^2, \tag{2.44}$$

where $v > v_0$. The dispersion relations for these cases are obtained as

$$\omega^2 = \omega_0^2 + v_0^2 k^2 \quad (\omega_0 = v_0/l) \tag{2.45}$$

and

$$\omega^2 = \tilde{\omega}_0^2 + v_0^2 k^2 \quad (\tilde{\omega}_0 = v_0/\tilde{l}) \tag{2.46}$$

respectively.

III. ESTIMATIONS OF THE AVERAGE SOLITON NUMBER DENSITY AND THE PARAMETER VALUES

The statistical mechanics of one-dimensional scalar fields governed by nonlinear wave equations having soliton solutions have already been developed by many authors.⁷⁻¹¹ Using those results the average soliton number density in our polynucleotide duplex is obtained as

$$\begin{aligned}
 n &= (N_k^\chi + N_{ak}^\chi + N_k^{\chi'} + N_{ak}^{\chi'})/L \\
 &= (2\pi)^{-1/2} (8/\tilde{l}) (\beta E_s^{(0)})^{1/2} e^{-\beta E_s^{(0)}},
 \end{aligned} \tag{3.1}$$

where N_k^χ , N_{ak}^χ , $N_k^{\chi'}$, and $N_{ak}^{\chi'}$ denote the number of χ kinks, χ antikinks, χ' kinks, and χ' antikinks of the uncoupled 2π solitons, respectively; L denotes the total length of our system and $E_s^{(0)}$ is the rest energy of the soliton. In the above expression, we assume that the uncoupled 2π solitons which have the lowest energy in the case $A \neq 0$ are only excited in the solvent condition where the H-D exchange measurements¹⁻³ were performed.

By dividing the double helix with total length L into N

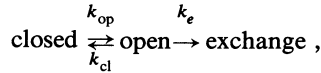
segments having a length of open configuration Δz , and denoting the number of segments in open configuration and closed configuration by N_{op} and N_{cl} , respectively, the equilibrium constant $K = N_{op}/N_{cl}$ can be written as

$$K = N_{op}/(N - N_{op}) \simeq N_{op}/N = nL/(L/\Delta z) = n \Delta z . \quad (3.2)$$

Using Eqs. (3.1) and (3.2), $\log_{10}K$ is given as

$$\log_{10}K = \log_{10}[(2\pi)^{-1/2}(8\Delta z/\tilde{l})] + \frac{1}{2}\log_{10}(\beta E_s^{(0)}) - \beta E_s^{(0)} \log_{10}e . \quad (3.3)$$

Teitelbaum and Englander⁴ and Nakanishi and Tsuboi³ postulated that the hydrogen-deuterium exchange reaction of double helical polynucleotides takes place as



where k_{op} is the rate constant for conformational opening, k_{cl} is that for reverse reaction (closing), and k_e is equal to the hydrogen exchange rate constant of the base residue that is completely exposed to the solvent. Postulating that $k_{op} + k_{cl} \gg k_e$, they calculated the equilibrium constant K from the observed H-D exchange rate constant k through an equation,

$$k = k_e \frac{k_{op}}{k_{op} + k_{cl}} = k_e \frac{K}{K + 1}$$

or

$$K = k/(k_e - k) .$$

The experimental data obtained by Nakanishi and Tsuboi³ and Teitelbaum and Englander⁴ in the temperature region lower than 47°C where double helical structure is kept as a whole are plotted in Fig. 8 on a logarithmic scale of K against reciprocal absolute temperature. By comparison between the theoretical result and the experimental data, we can estimate the energy of the soliton, the length of open configuration, and the parameter values in our theory as follows. The value of $E_s^{(0)}$ can be determined as that slope of the theoretical curve, which is obtained from Eq. (3.3), reproduces that of the line (l) in Fig. 7; thus we obtain (in eV)

$$E_s^{(0)} = 0.35 . \quad (3.5)$$

The constant term of the right-hand side of Eq. (3.3) can be determined by substituting the value of $E_s^{(0)}$ into Eq. (3.3) and the coordinates of one arbitrary point on the line (l) (for example, $\log_{10}K = -3.50$ at $1/T \times 10^3 = 3.22$) into Eq. (3.3). From this we get $\log_{10}[(2\pi)^{-1/2}(8\Delta z/\tilde{l})] = 1.60$, which corresponds to the entropy change $\Delta S = 7.3$ e.u.; we then have $\Delta z/\tilde{l} = 12.5$. This shows excellent agreement with the length of open configuration $\Delta z \simeq 10\tilde{l}$ which is estimated from the theoretical $\tilde{\phi}_s$ -versus- ξ/\tilde{l} curve. If we assume $2(A+B) \simeq 4S$, we can estimate the H-bonding energy and the sum of the stacking and torsional energies (in eV) by using the relations $E_s^{(0)} = 8[(A+B)S]^{1/2}$ in Eqs. (2.36) and (3.5) as follows:

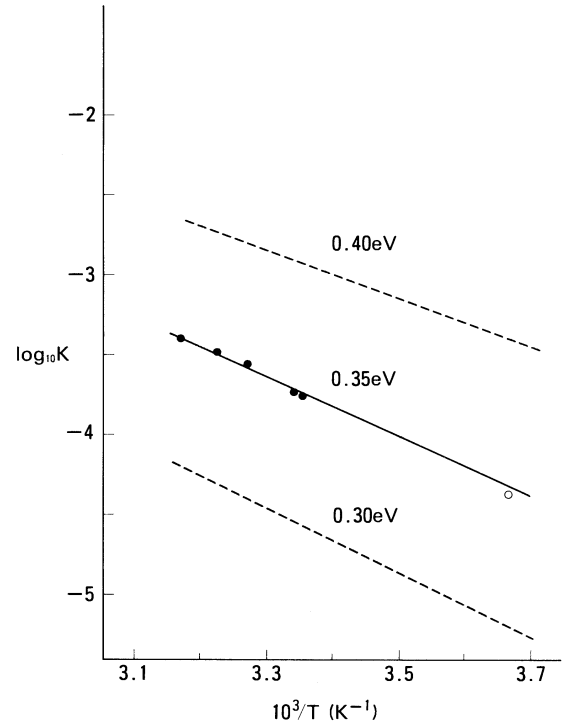


FIG. 8. Equilibrium constant of closed and open forms of double-helical polynucleotide [poly(γ I), poly(γ C)] on a logarithmic scale ($\log_{10}K$) plotted against reciprocal absolute temperature. ●, determined by stopped-flow ultraviolet spectroscopy by Nakanishi and Tsuboi; ○, determined by Sephadex column chromatography by Teitelbaum and Englander. Theoretical curves obtained from Eq. (3.3) assuming $\Delta z = 12.5\tilde{l}$ are shown by the dashed curves which correspond to $E_k^{(0)} = 0.30, 0.35$, and 0.40 eV, respectively.

$$2(A+B) \simeq 0.12, \quad 4S \simeq 0.12 . \quad (3.6)$$

Though the H-bonding energy $2(A+B) \simeq 0.12$ eV which we estimate here seems too small, this value corresponds to the difference between the H-bonding energy between the base pair and that between the base and the water molecules of the solvent. From Eqs. (2.25) and (3.6) we obtain $\tilde{l} \simeq 0.7a$. Then we can estimate the length of open configuration and the upper limit of soliton velocity as follows, assuming an approximate mean value of the moment of inertia of nucleotide $I = MR^2$, $M = 308m_p$, $R \simeq 4 \text{ \AA}$:

$$\Delta z \simeq 12.5\tilde{l} = 8.9a , \quad (3.7)$$

$$v_0 \simeq 8.3 \times 10^3 \text{ cm/sec} .$$

From the experimental data in Fig. 8, we can see that $K \simeq 2 \times 10^{-4}$ at 300 K; then we can estimate soliton number density as

$$n \simeq K/\Delta z \simeq 2 \times 10^{-5}/a \quad (3.8)$$

at 300 K. The mean number density of bases in open state is then about $5n \simeq 10^{-4}/a$.

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