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Phase transition of a quasi-one-dimensional system

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The statistical mechanics of the quasi-one-dimensional system of DNA is studied with the Morse and Deng-Fan potentials for the interstrand hydrogen bonds of nucleotide pairs. The intrastrand interactions between nucleotides are characterized by a simple harmonic potential in which the coupling strength has a significant effect on the phase transition of the DNA system.

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I. INTRODUCTION

Phase transitions are fascinating physical phenomena of systems that undergo structural changes due to changes in the degrees of freedom or symmetry. To describe the phenomena, it is advantageous to consider exactly solvable models with the underlying mechanisms as approximations, such that corrections to the models may then be made to account for any experimental discrepancies.

In this paper, we shall study the denaturation of the quasi-one-dimensional system of the DNA double helix with two exactly solvable potentials. The two DNA strands are held together by double and triple hydrogen bonds depending on the types of nucleotide base pairs in the strands. For simplicity, we shall consider an average interaction strength between the strands. As an application, we may consider poly(A-T)-poly(A-T) DNA. The intrastrand interactions are of the covalent type and are much stronger than the hydrogen bonds. In this sense, the DNA helix forms a quasi-one-dimensional structure.

The subject of the denaturation of DNA has had a long history [1], with theoretical studies based on the Ising model, in which each base pair is assumed to be either open (broken) or intact. A more sophisticated approach is the lattice dynamical theory, which is based on the modified self-consistent phonon approach introduced in 1984 [2] with the real configurations of DNA molecules given by experiment, and assumed harmonic potentials for the nonhydrogen bonds and Morse potentials for the hydrogen bonds. However, for tractable calculations, a linear lattice dynamical theory has generally been considered with Morse potentials replaced by harmonic ones.

It is well known that a useful DNA model must be nonlinear in nature. The introduction of the idea of nonlinear excitations with soliton theories [3] suggested a plausible explanation of the open states of DNA. In these theories, statistical mechanics was not considered and the results do not represent the thermal denaturation of DNA. The Peyrard and Bishop (PB) model was introduced in 1989 [4] to take into account the thermal effect. It consists of two sets of degrees of freedom (u_n and v_n) corresponding to the transverse displacements of the bases, i.e., displacements along the direction of the hydrogen bonds connecting the two bases in a pair. Harmonic coupling is assumed for the neighboring bases along the strands with a common coupling constant k and mass M for each base. In the PB model, the Morse potential [5] is used for the interstrand hydrogen bonds. Many subsequent studies [6,7] of the denaturation of DNA have been based on this model.

In the following sections, we shall study the Morse potential and the Deng-Fan potential [8] for the interstrand hydrogen bonds by calculating the delocalization or melting temperatures and the interstrand quantities as a function of temperature. The effects of the intrastrand interactions on the interstrand quantities will be mentioned.

II. QUASI-ONE-DIMENSIONAL SYSTEM OF DNA

Let $x_n=(u_n+v_n)/\sqrt{2}$ and $y_n=(u_n-v_n)/\sqrt{2}$, the interstrand separation of the base pair being $\sqrt{2}y_n$. We shall assume that the DNA helix consists of N nucleotide base pairs. The Hamiltonian for the system has the form

$$H=\sum_{n=1}^{N}\left\{\frac{p_n^2}{2M}+\frac{q_n^2}{2M}\right\}+H'(x_n,x_{n-1})+f(y_n,y_{n-1}), \tag{1}$$

where

$$H'(x_n,x_{n-1})=\sum_{n=1}^{N}\frac{1}{2}k(x_n-x_{n-1})^2,$$

$$f(y_n,y_{n-1})=\sum_{n=1}^{N}\left\{\frac{1}{2}k(y_n-y_{n-1})^2+V(y_n)\right\}, \tag{2}$$

$p_n=M\dot{x}_n$ and $q_n=M\dot{y}_n$ are the canonical momenta, and $V(y_n)$ is the interstrand potential for the hydrogen bonds between nucleotide pairs. The statistical mechanics of the model is described by the partition function ($\beta=1/k_BT$)

$$\mathcal{Z}=\int_{-\infty}^{+\infty}\prod_{n=1}^{N}dx_ndy_ndp_ndq_ne^{-\beta H(p_n,x_n,q_ny_n)}\equiv\mathcal{Z}_x\mathcal{Z}_y\mathcal{Z}_p\mathcal{Z}_q, \tag{3}$$

where k_B is Boltzmann's constant. We have imposed periodic boundary conditions on the variables. The integrals of the variables p_n,q_n,x_n are of Gaussian type and give

$$\mathcal{Z}_p=\mathcal{Z}_q=(2\pi Mk_BT)^{N/2},\quad \mathcal{Z}_x=(2\pi k_BT/k)^{N/2}. \tag{4}$$

The remaining configurational partition function $\mathcal{Z}_y$ involves the nonlinear interstrand potential,

$$\mathcal{Z}_y=\int_{-\infty}^{+\infty}\prod_{n=1}^{N} dy_n e^{-\beta f(y_n,y_{n-1})}, \tag{5}$$

which can be evaluated by using the transfer-integral method [9] with each integral being defined by

$$\int dy_{n-1}e^{-\beta f(y_n,y_{n-1})}\varphi(y_{n-1})=e^{-\beta\epsilon_i}\varphi(y_n). \tag{6}$$

By expanding $\varphi(y_{n-1})$ in Eq. (6) about y_n, we are led, in the continuum limit, to the following Schrödinger-type equation:

$$-\frac{1}{2\beta^2 k}\frac{d^2\varphi_i(y)}{dy^2}+U_{\text{eff}}(y,\beta)\varphi_i(y)$$
$$=\epsilon_i\varphi_i(y),\quad i=0,1,2,\ldots, \tag{7}$$

where φ_i is an eigenfunction with corresponding eigenenergy ϵ_i, and $U_{\text{eff}}(y,\beta)$ is a temperature-dependent effective potential,

$$U_{\text{eff}}(y,\beta)=V(y)+\frac{1}{2\beta}\ln\left(\frac{\beta k}{2\pi}\right). \tag{8}$$

The Schrödinger equation is dependent on the harmonic coupling constant k which defines the intrastrand nucleotide interactions. The solvability of Eq. (7) depends on the interstrand potential $V(y)$, for which we shall consider the Morse and Deng-Fan potentials. Equation (7) also has an effective mass $M_{\text{eff}}\equiv\beta^2 k\hbar^2$ ($\hbar$ is Planck's constant). As $M_{\text{eff}}\rightarrow\infty$, one expects that the system should be in the condensed phase; this happens when $T\rightarrow 0$ or $k\rightarrow\infty$. For the DNA system to be in the condensed phase, we require that $T<T_d$, where T_d is the delocalization or melting temperature, and as $k\rightarrow\infty$ the system exhibits only the condensed phase for all finite temperatures.

The phase transition of the DNA system is characterized by the detachment of the two strands. Hence a measure for the transition can be defined by the average

$$\langle y^m\rangle=\frac{\sum_{n=0}^{N}\langle\varphi_n(y)|y^m|\varphi_n(y)\rangle e^{-N\beta\epsilon_n}}{\sum_{n=0}^{N}\langle\varphi_n(y)|\varphi_n(y)\rangle e^{-N\beta\epsilon_n}}, \tag{9}$$

where m is a positive integer. The first-order average ($m=1$) gives the mean stretching $\sqrt{2}\langle y\rangle$ of the hydrogen bonds as a function of temperature, while the second-order average ($m=2$) gives the variance of the separation of the two strands and provides a simple measure for the difference between the two potentials.

We expect that the mean stretching $\sqrt{2}\langle y\rangle$ and higher-order quantities $\langle y^m\rangle$ ($m=2,3,\ldots$) increase with temperature and diverge when $T=T_d$. Since we are interested in the thermodynamic limit ($N\rightarrow\infty$), the dominant contribution comes from the ground state $\varphi_0(y)$ below the melting temperature. For the purpose of comparison, we shall calculate the first two orders

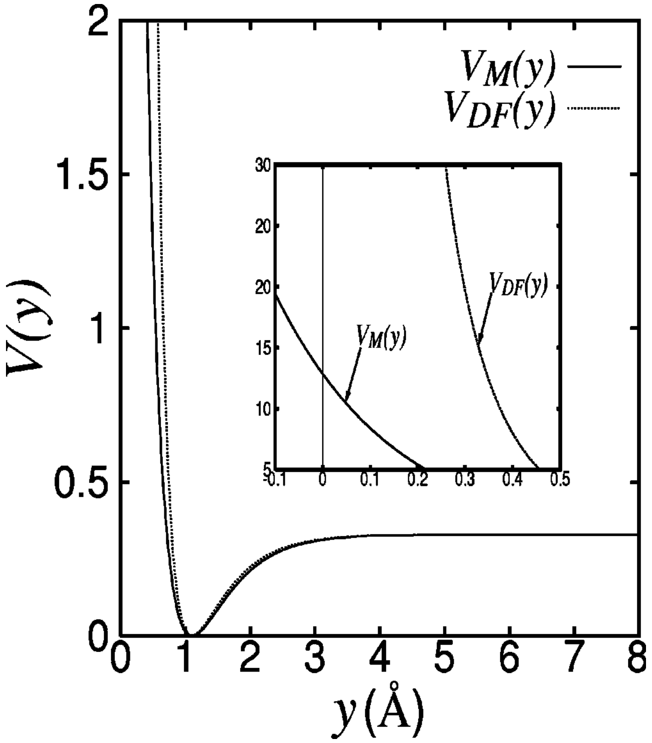

FIG. 1. The Morse potential $V_M(y)$ and the Deng-Fan potential $V_{DF}(y)$ are plotted with $D=0.33$ eV, $a=1.8$ Å^{-1}, $k=3\times10^{-3}$ eV/Å^2, and $r_e=1.1$ Å. The inset shows that the Morse potential remains finite for unphysical negative values of y.

$$\langle y^m\rangle=\int\varphi_0^2(y)y^m dy,\quad m=1,2, \tag{10}$$

for the Morse and Deng-Fan potentials.

A. The Morse potential

We first consider the Morse potential for the interstrand base pairs

$$V(u_n-v_n)=D[e^{-a(u_n-v_n-r_e)}-1]^2,$$
$$-\infty<u_n,\quad v_n<\infty, \tag{11}$$

where we shall use the values for the parameters D and a from [4], $D=0.33$ eV, $a=1.8$ Å^{-1}, and the following values for the coupling constant k: (a) 2×10^{-3} eV/Å^2, (b) 3×10^{-3} eV/Å^2, (c) 4×10^{-3} eV/Å^2. The constant $r_e=1.1$ Å denotes the equilibrium separation of the base pairs. This potential is plotted in Fig. 1 with $k=3\times10^{-3}$ eV/Å^2.

We define $x_n=(u_n+v_n)/\sqrt{2}$ and $y_n=(u_n-v_n)/\sqrt{2}$, and let $(\sqrt{2}y_n-r_e)=\sqrt{2}r$. Then the Schrödinger equation (7) has the effective potential

TABLE I. Melting temperatures $T_d^{(n)}$ $(n=0,1,2)$ of DNA with $D=0.33$ eV, $a=1.8$ Å^{-1} and three values for k.

Potential		k(eV/Å^2) 2×10^{-3}	 3×10^{-3}	 4×10^{-3}
Morse	$T_d^{(0)}$ (K)	331.25	405.70	468.46
	$T_d^{(1)}$ (K)	110.42	135.23	156.15
	$T_d^{(2)}$ (K)	66.25	81.14	93.69
Deng-Fan	$T_d^{(0)}$ (K)	288.27	353.06	407.68
	$T_d^{(1)}$ (K)	97.02	118.83	137.21
	$T_d^{(2)}$ (K)	59.67	73.09	84.39

$$U_{\mathrm{eff}}(r,\beta)=D[e^{\sqrt{2}ar}-1]^2+\frac{1}{2\beta}\ln\left(\frac{\beta k}{2\pi}\right). \tag{12}$$

Equation (7) with this effective potential can be solved exactly and has eigenfunctions and eigenenergies as follows [4,10]:

$$\varphi_n=N_n e^{-\xi/2}\xi^s F(-n,2s+1,\xi),\quad n=0,1,2,\ldots, \tag{13}$$

$$\epsilon_n=\frac{1}{2\beta}\ln\left(\frac{\beta k}{2\pi}\right)+\frac{2a}{\beta}\sqrt{\frac{D}{k}}\left(n+\frac{1}{2}\right)-\frac{a^2}{\beta^2 k}\left(n+\frac{1}{2}\right)^2, \tag{14}$$

where

$$N_n=\left[\frac{2\sqrt{2}as}{n!\,\Gamma(2s+n+1)}\right]^{1/2}\frac{(2s+n)!}{(2s)!} \tag{15}$$

is the normalization constant, $\xi=2de^{-\sqrt{2}ar}$, $d=(\beta/a)\sqrt{kD}$, $s=d-n-\frac{1}{2}$, and

$$\begin{aligned}F(-n,2s+1,\xi)=1&+\frac{(-n)\xi}{2s+1}+\frac{(-n)(-n+1)}{(2s+1)(2s+2)}\frac{\xi^2}{2!}+\cdots\\&+\frac{(-n)(-n+1)\cdots1}{(2s+1)(2s+2)\cdots(2s+1+n)}\\&\times\frac{\xi^n}{n!}+\cdots.\end{aligned} \tag{16}$$

The existence of bound states requires that the parameter s be positive. Then the number of bound states n must take only positive integral values from zero to the greatest value for which $d>n+1/2$. The temperature for the existence of the nth bound state is defined by

$$T<\frac{2\sqrt{kD}}{(2n+1)ak_B}=T_d^{(n)},\quad n=0,1,2,\ldots, \tag{17}$$

where $T_d^{(n)}$ denotes the melting temperature of the nth state. The melting temperatures $T_d^{(n)}$ $(n=0,1,2)$ are listed in Table I with the values $D=0.33$ eV, $a=1.8$ Å^{-1}, and three values for k. The melting temperature of the ground state is very much higher than for the excited states, which therefore play no significant role in the determination of the interstrand separation. In the thermodynamic limit, the ground state dominates with the normalized eigenfunction

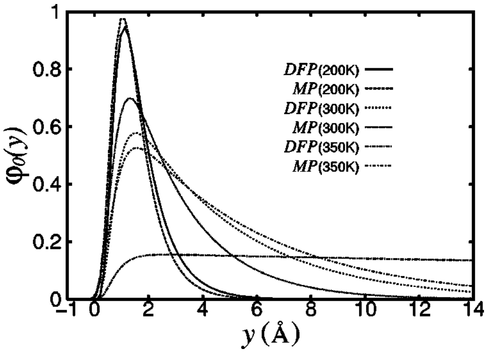

FIG. 2. The ground state eigenfunctions in the Morse potential (MP) and the Deng-Fan potential (DFP) are plotted with $k=3\times10^{-3}$ eV/Å^2 and for several temperatures.

$$\begin{aligned}\varphi_0(r)=(\sqrt{2}a)^{1/2}&\frac{(2d)^{d-1/2}}{[\Gamma(2d-1)]^{1/2}}\exp(-de^{-\sqrt{2}ar})\\&\times\exp\left[-\left(d-\frac{1}{2}\right)\sqrt{2}ar\right]\end{aligned} \tag{18}$$

and eigenenergy

$$\epsilon_0=\frac{1}{2\beta}\ln\left(\frac{\beta k}{2\pi}\right)+\frac{a}{\beta}\left(\frac{D}{k}\right)^{1/2}-\frac{a^2}{4\beta^2 k}. \tag{19}$$

The ground state wave function is plotted in Fig. 2 with $k=3\times10^{-3}$ eV/Å^2 and for the temperatures 200, 300, and 350 K.

The averages $\langle y\rangle$ and $\langle y^2\rangle$ as a function of temperature are calculated by

$$\langle y^m\rangle=\int_{-\infty}^{+\infty}\varphi_0^2(y)y^m dy, m=1,2, \tag{20}$$

where $y=r+r_e/\sqrt{2}$. The results are plotted, respectively, in Figs. 3 and 4 for $k=2\times10^{-3}$, $k=3\times10^{-3}$, and and $k=4\times10^{-3}$ eV/Å^2.

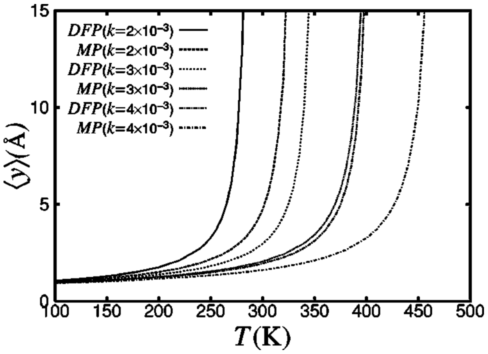

FIG. 3. The average $\langle y\rangle$ of the ground state in the Morse and Deng-Fan potentials is plotted as a function of temperature for three values of k.

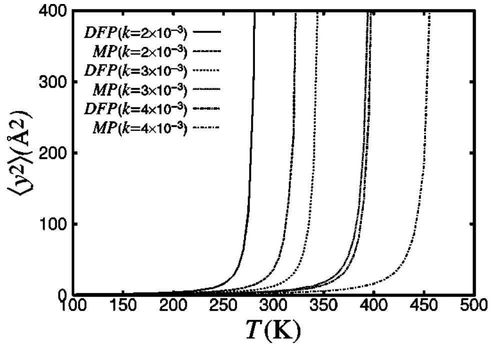

FIG. 4. The average $\langle y^2\rangle$ of the ground state in the Morse and Deng-Fan potentials is plotted as a function of temperature for three values of k.

B. The Deng-Fan potential

We next consider the Deng-Fan (DF) or generalized Morse potential [8]

$$V(u_n-v_n)=D\left[1-\frac{b}{e^{a(u_n-v_n)}-1}\right]^2,\qquad 0<u_n-v_n<\infty, \tag{21}$$

where $b=e^{ar_e}-1$, and D, a, and r_e are constants as defined in the Morse potential. Unlike the Morse potential, the DF potential is defined only for positive values of $y_n=u_n-v_n$. As plotted in Fig. 1, the DF potential has a slightly harder core and a narrower potential well than the Morse potential. We expect a harder core to give a lower delocalization temperature, since the ground state in the DF potential will be pushed more to positive separation than that in the Morse potential. This difference can be seen in Fig. 2.

The Schrödinger equation has the effective potential

$$U_{\rm eff}(y,\beta)=D\left[1-\frac{b}{e^{\sqrt{2}ay-1}}\right]^2+\frac{1}{2\beta}\ln\left(\frac{\beta k}{2\pi}\right). \tag{22}$$

Let

$$r=1/(e^{\sqrt{2}ay}-1),$$

$$m=k\beta^2D/a^2,$$

$$\ell=(1+\sqrt{1+4mb^2})/2,$$

$$\alpha_n=[mb(b+2)/(n+\ell)-(n+\ell)]/2$$

and $\beta_n=\alpha_n+n+\ell$.

The wave functions and energies, respectively, read [11]

$$\varphi_n(r)=N_nr^{\alpha_n}(1+r)^{-\beta_n}{}_2F_1\times(-n,-n+1-2\ell;2\alpha_n+1;-r), \tag{23}$$

$$\epsilon_n=s_0+D-\frac{a^2\alpha_n^2}{k\beta^2},\quad n=0,1,2,\ldots, \tag{24}$$

where

$$N_n=\left[\frac{\sqrt{2}a(\alpha_n+n+\ell)\Gamma(2\alpha_n+n+1)\Gamma(2\alpha_n+n+2\ell)}{n!(n+\ell)\Gamma(2\alpha_n)\Gamma(2\alpha_n+1)\Gamma(n+2\ell)}\right]^{1/2}$$

is the normalization constant and

$${}_2F_1(a,b;c;r)=\sum_{n=0}^{\infty}\frac{(a)_n(b)_n}{(c)_n}\frac{r^n}{n!},\quad (a)_n=\frac{(a+n-1)!}{(a-1)!}, \tag{25}$$

is the hypergeometric function. For bound states, we must have integral values n such that $n<\sqrt{mb(b+2)}-\ell$, which gives

$$\ell\geqslant\frac{1}{4}(b+2+2nb)+\frac{1}{4}\sqrt{b(b+2)(2n+1)^2+2b+4}\equiv\ell_+.$$

Thus, for the nth bound state, we must have a temperature such that

$$T<\frac{\sqrt{kD}}{ak_B}\frac{b}{\sqrt{\ell_+(\ell_+-1)}}\equiv T_d^{(n)}, \tag{26}$$

where $T_d^{(n)}$ denotes the melting temperature of the nth state. For the first three states, the temperatures $T_d^{(n)}$ $(n=0,1,2)$ are tabulated in Table I.

In the thermodynamic limit, we need to consider only the ground state with eigenfunction and eigenenergy

$$\varphi_0(r)=N_0r^{\alpha_0}(1+r)^{-\beta_0},\quad \epsilon_0=\frac{1}{2\beta}\ln\left(\frac{\beta k}{2\pi}\right)+D-\frac{a^2\alpha_0^2}{k\beta^2}, \tag{27}$$

where

$$N_0=\left[\frac{\sqrt{2}a\beta_0\Gamma(2\beta_0)}{\ell\Gamma(2\alpha_0)\Gamma(2\ell)}\right]^{1/2},\quad \alpha_0=\frac{1}{2}\left[\frac{mb(b+2)}{\ell}-\ell\right],$$

$$\beta_0=\alpha_0+\ell. \tag{28}$$

To describe the state of DNA below the melting temperature, the ground state is used to calculate the averages

$$\langle y^m\rangle=\int_0^{+\infty}\varphi_0^2(y)y^m dy,\quad m=1,2,$$

where $y=\ln(1+1/r)/\sqrt{2}a$. These averages are plotted in Figs. 3 and 4 as a function of temperature for $k=2\times10^{-3}$, $k=3\times10^{-3}$, and $k=4\times10^{-3}$ eV/Å^2.

III. CONCLUSIONS

The main physical property of the phase transition in the quasi-one-dimensional system of DNA is characterized by the detachment of the DNA strands. Thus, we have calculated the ground state wave functions and the interstrand quantities $\langle y\rangle$ and $\langle y^2\rangle$ as a function of temperature.

The ground state eigenfunctions are plotted in Fig. 2 for several temperatures. At low temperatures, the peaks of the ground states are centered at about the equilibrium separation $r_e = 1.1$ Å. As the temperature increases, the ground state wave functions become less localized, and the wave function in the DP potential delocalizes before that in the Morse potential.

Table I indicates that for the same melting temperature a smaller k is needed for the Morse potential than for the Deng-Fan potential. In particular, $k = 3 \times 10^{-3}$ eV/Å^2 for the Morse potential gives $T_d = 405.70$ K, while $k = 4 \times 10^{-3}$ eV/Å^2 for the Deng-Fan potential gives $T_d = 407.68$ K. This feature is also reflected in Figs. 3 and 4, where the Morse potential with $k = 3 \times 10^{-3}$ eV/Å^2 gives about the same physical aspects as the DF potential with $k = 4 \times 10^{-3}$ eV/Å^2. Therefore, a stronger intrastrand coupling is needed for the DF potential.

The melting temperature T_d is seen to behave as $T_d \propto \sqrt{k}$. Thus, if the coupling strength of the covalent bonds along the DNA strands increases indefinitely, one of the two dimensions freezes out and the system becomes one dimensional. In essence, this corresponds to an infinite effective mass M_{eff} in the Schödinger equation, and we expect no denaturation. Thus, the transition depends on the intrastrand dimension, although the detachment of the strands occurs in the interstrand dimension.

We mention that other solvable potentials that exhibit thermal denaturation can be considered. For example, in [12] a potential based on the superalgebra formalism was studied; this potential has a very different form from the potentials studied here. All exactly solvable potentials provide only approximations to the real DNA system. A comparative study of solvable potentials should provide useful understanding of the dynamics of DNA.

Finally, we note that in order to account for other effects, such as the stacking energy between two neighboring base pairs, a modified model with an anharmanic potential for nonhydrogen bonds has been considered in conjunction with the Morse potential [6,7]. However, solving this system requires numerical methods, and the determination of all the parameters in the model for comparing the theory with experiments is still outstanding. Also, a more useful model should include the effect of the heterogeneous sequence composition of DNA [13].

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