Analytic results of the DNA thermal denaturation in the Peyrard-Bishop-Dauxois model

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Abstract. The thermal denaturation of the DNA within the Peyrard-Bishop-Dauxois (PBD) model is analyzed analytically through the variational method adapted to determine the ground state energy of a Schrödinger-like equation with position-dependent mass. The approach is used to determine the melting temperature of the DNA. The results are compatible to experimental data.

1. Introduction

More than sixty years ago a structural model for the DNA molecule was proposed [1] in which two strands of nucleotides in helix form are linked by hydrogen bonds containing genetic information in specific basis pairs. The separation of the DNA double helix is an important effect on the transcription and replication processes of the molecule since in these cases it is necessary to expose the nitrogenous bases to the solution. This implies the need of large amplitudes and highly localized movements, indicating that the molecule dynamics should be nonlinear.

Several models have been proposed to describe the DNA [2], among which stands out the Peyrard - Bishop model, (PB), proposed in 1989 to study the thermal denaturation of the molecule through statistical mechanics and its nonlinear dynamics [3]. The model consists of two chains of particles coupled by nonlinear springs described by the Morse potential, simulating the hydrogen bonds that connect the two basis in a pair. The main feature of this model is to describe the separation of double-stranded DNA in terms of an order parameter which is usually the mean stretch of the base pairs. This model was used to exploit various dynamic and thermodynamic aspects of DNA as soliton propagation, [3], [4], wall domain formation [5], power location [6] and the formation and stability of breathers, [7]-[9].

Even though the PB model provides quantitatively a good description of the DNA thermal denaturation [10], the behavior of the order parameter as a function of temperature provides a curve for the phase transition that is not as abrupt as the experimental results indicate. Several modifications of this model have been attempted with the aim of improving the description of the phase transition of the DNA molecule. One of the proposed amendments was to modify the stacking interaction, [11]-[13]. Thus, in the Peyrard-Bishop-Dauxois model of DNA [11], (PBD), an additional exponential term is attached to the purely harmonic potential used to simulate the stacking interaction in the previous PB model [3].
The thermodynamic properties of the denaturation of both, the PB model and the PBD model, may be obtained with the transfer integral operator method (TI), [14]. This technique allows relating the partition function of the system with the eigenvalues of a linear second order differential equation similar to the Schrödinger equation. For the PB model this equation has exact analytic solution [3, 10], whereas for the PBD model the full transfer operator formalism leads to a Schrödinger-like equation, but with position-dependent mass [15]. In both approaches, the spectrum of the TI operator, in the thermodynamical limit, is dominated by the lowest eigenvalue and the thermodynamic quantities, such as the mean stretching $< y >$ of the Hydrogen bonds, for both models (PB and PBD), was analysed numerically. Thus, the aim of the present work is to evaluate analytically the mean stretching $< y >$ of the Hydrogen bonds in the PBD model. In short, the problem is to solve analytically a linear second order differential equation that is formally equal to a Schrödinger equation with a position-dependent mass. The Schrödinger equation with position-dependent mass appears in several fields of physics such as in the studies of semiconductors [16], H clusters [17], quantum wells and quantum dots [18]-[19] and polarons [20]. In these kind of quantum systems, the mass does not commute with the momentum, which leads to the problem of the operator ordering inside the kinetic energy operator [21]-[24]. Several methods can be used in order to obtain the solution of the position-dependent mass problem, for example, the point canonical transformation (PCT) [25]-[27] and the supersymmetric quantum mechanics formalism, [28]-[30].

For the present case, as the interest is in the ground state, it appears that the variational method could perfectly be applied to the PBD model, allowing the evaluation of its thermodynamic properties. Through an adaptation of the variational model we were able to evaluate the ground state solution of the Schrödinger-like equation with a position-dependent mass and thus evaluate analytically the mean stretching $< y >$ of the Hydrogen bonds in the PBD model. The DNA molecule phase transition thus obtained is at a temperature compatible with the displayed for the macromolecule in the literature [15], [31].

In the sequence the general sketches of the PBD model and the adapted variational method are presented followed by the calculation of the mean stretching $< y >$ as a function of the temperature.

2. The Peyrard, Bishop & Dauxois Model (PBD)
The PBD model [11] was proposed as a phenomenological extension of the PB model [3] with the purpose of improving the phase transition description of the DNA molecule. Thus, an exponential term was introduced to the purely harmonic term of the stacking interactions. According to the authors, [11], this term was added due to the observation that the stacking energy is a property of the base pairs and not of the individual bases. The change of the stacking interaction leaves the phase transition curve more abrupt, which agrees qualitatively with the DNA molecule denaturation properties observed experimentally [11]. The Hamiltonian for the PBD model is given by

$$\begin{align*}
H &= \sum_i \left( \frac{p_i^2}{2m} + V(y_i) + W(y_i, y_{i-1}) \right).
\end{align*}$$

The first term of equation (1) is the kinetic energy of base pairs with momentum $p_i = m \frac{dy_i}{dt}$, where $m = 300 \ u$ is the average mass of nucleotides; the second term is the Morse potential which represents the hydrogen bonds of the molecule, as well as the repulsive interactions between the phosphate groups and solvent effects. The DNA stacking interactions are represented by $W(y_i, y_{i-1})$ which is given by

$$W(y_i, y_{i-1}) = \frac{k}{2} \left( 1 + \rho e^{-\alpha(y_i + y_{i-1})} \right) (y_i - y_{i-1})^2,$$

(2)
where \( y_i \) represents, as usual, the stretching the \( i-th \) pair of bases connected by hydrogen bonds. Thus, the term that multiplies \( (y_i - y_{i-1})^2 \) varies between \( \frac{\kappa}{2} (1 + \rho) \) and \( \frac{\kappa}{2} \), where \( \kappa \) is the elastic constant of the interaction alongside the chain; it is added in order to show the decrease effect of the stacking interactions with the weakening of the hydrogen bond, [11].

The TI operator method for this Hamiltonian allows us to establish a relationship between the statistical mechanics problem of finding the partition function of the system with eigenfunctions and energy eigenvalues of a linear second order differential equation, given by

\[
\left\{ -\frac{1}{2\beta^2\kappa D g(y_i)} \frac{d^2}{dy_i^2} + U(y_i) \right\} \Psi_n(y_i) = \bar{\varepsilon}_n \Psi_n(y_i),
\]

where

\[
g(y_i) = (1 + \rho e^{-2\alpha y_i}),
\]

\[
DU(y_i) = V(y_i) + \frac{1}{2\beta} \ln[g(y_i)],
\]

\[
D\bar{\varepsilon}_n = \varepsilon_n + \frac{1}{2\beta} \ln\left( \frac{2\pi a^2}{\beta\kappa} \right),
\]

with \( D \) and \( a \) are parameters of the Morse potential,

\[
V(y_i) = D(e^{-\alpha y_i} - 1)^2;
\]

\( \varepsilon_n \) are the energy eigenvalues, \( \beta = \frac{1}{k_BT} \), \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \kappa \) and \( \rho \) are parameters of the potential representing stacking interactions (2) and \( y_i \) is the stretching the \( i-th \) pair base of the oscillators chain.

Equation (3) is a Schrödinger-like equation with position-dependent mass, \( (m(y_i) \propto g(y_i)) \), whose solutions can be used to evaluate some thermodynamic properties of the PBD lattice, i.e., the eigenfunctions \( \Psi(y) \) of equation (3) can be used to determine the phase transition curve for the PBD model, through the evaluation of the mean stretching \( \langle y \rangle \) in terms of the temperature, given by

\[
\langle y \rangle = \int_{-\infty}^{+\infty} y |\Psi(y)|^2 dy
\]

which shows at which temperature the DNA denaturation takes place. However, unlike what happens with the similar equation of the PB model, it is not possible to determine its exact analytic solutions. Thus, we propose an analytical method to solve it, based on a modified version of the variational method.

To find the lowest energy solution of equation (3) is precisely what we need since in the thermodynamic limit the contribution of excited states can be neglected.

The fact that we are interested in the lowest energy level of equation (3) makes the variational method particularly useful, even though there must be changes in order to apply it. In what follows, we devise this methodology to apply in the PBD model.

3. Variational Method Adapted to systems with position-dependent mass

The variational method is an analytic approximated method used to solve the Schrödinger equation, [32]-[37]. It consists on the choice of an eigenfunction (\( \Psi_\mu \)), the trial function that depends on a parameter \( \mu \) or a set of parameters \( \{\mu\} \), used to compute the energy eigenvalue. The variational principle guarantees that the mean energy obtained from this trial function is always an upper limit of the real ground state energy of the system (\( E_0 \)). The lowest energy is equal to \( E_0 \), if the trial function is the exact solution of the Schrödinger equation. The variational parameters in \( \Psi_\mu \) are varied until the expectation value of the energy is minimum.
In systems with position-dependent mass, the essence of the variational method remains the same, but the structure should be adapted. The Schrödinger-like equation to this kind of problem can be written generally as:

\[ -\frac{\hbar^2}{2m(y)} \frac{d^2\Psi(y)}{dy^2} + V(y)\Psi(y) = E\Psi(y), \]  

where the mass \( m(y) \) has position-dependence, \( V(y) \) is the potential and \( E \) is the energy eigenvalue of the system. Equation (7) can be rewritten if we multiply all the terms of the equation by \( \frac{2}{\hbar^2}m(y) \). This procedure leads to the equation,

\[ -\frac{d^2\Psi(y)}{dy^2} + \frac{2m(y)}{\hbar^2}(V(y) - E)\Psi(y) = 0. \]  

The term \( \frac{2m(y)}{\hbar^2}(V(y) - E)\Psi(y) \) can be separated in a term depending on the position and a constant term, which defines the effective potential \( V_{eff} \),

\[ V_{eff} = \frac{2m(y)}{\hbar^2}(V(y) - E). \]  

Thus, equation (8) is rewritten as the following effective equation,

\[ H_{eff}\Psi(y) = \lambda\Psi(y) \]  

where \( H_{eff} \) is the effective Hamiltonian operator, given by

\[ H_{eff} = -\frac{d^2}{dy^2} + V_{eff}. \]  

and \( \lambda \) is the eigenvalue of the differential equation (10). In this case, from equation (8), \( \lambda \) is fixed and it is equal to zero.

The variational method should be adapted to solve equation (8) due to the fact that the energy eigenvalue of the Schrödinger-like equation (7) is inserted in the effective potential \( V_{eff} \) and the term that originally is interpreted as the energy eigenvalue is now a fixed constant zero. Thus, the adopted procedure is to vary the energy eigenvalue \( E \), and consequently to vary the effective potential in order to compute the mean energy, as usual in the variational method,

\[ <H_{eff}> = \frac{\int_V \Psi_\mu^* H_{eff} \Psi_\mu dV}{\int_V \Psi_\mu^* \Psi_\mu dV} \]  

where \( H_{eff} \) is the effective Hamiltonian given by (11), \( \Psi_\mu \) is the trial function and \( \mu \) is the variational parameter. Notice that the value of the mean energy \( <H_{eff}> \) is a function of the energy eigenvalue \( E \) and the variational parameter \( \mu \), \( f(E,\mu) \), i.e.,

\[ <H_{eff}> = \frac{\int_{-\infty}^{+\infty} \Psi_\mu^*(y)(-\frac{d^2\Psi_\mu(y)}{dy^2} + V_{eff})\Psi_\mu(y)dy}{\int_{-\infty}^{+\infty} \Psi_\mu^*(y)\Psi_\mu(y)dy} = f(E,\mu), \]  

and, from equation (8), the value of \( <H_{eff}> \) is zero. Then, after integrating (13), the minimum energy \( E_{min} \) is found for the particular value of the variational parameter \( \bar{\mu} \) that it satisfies

\[ f(E_{min},\bar{\mu}) = 0. \]  

This value can be found through a graphic representation of \( <H_{eff}> \) versus \( \mu \). The minimum energy \( E_{min} \) is obtained from the intersection point where \( <H_{eff}> = 0 \).

In what follows we apply the approach the PBD model, restricting the approach to only one variational parameter.
4. The variational method applied to the PBD model
To determine the thermodynamic properties of the model we use the adapted variational method and find the wave function that is a solution of equation (3), which is necessary to evaluate the mean stretch behavior of the base pairs as a function of temperature, i.e., \( < y > \) for various temperatures.

The first step is to multiply all terms of equation (3) for \( g(y_i) \) and constants, which leads to an equation similar to (8)

\[
\left\{ -\frac{d^2}{dy_i^2} + 2\beta^2 \kappa D g(y_i)(U(y_i) - \bar{\varepsilon}_n) \right\} \Psi_n(y_i) = 0,
\]

and which can be written in terms of an effective potential \( V_{eff} \),

\[
\left\{ -\frac{d^2}{dy_i^2} + V_{eff} \right\} \Psi_n(y_i) = 0
\]

where

\[
V_{eff} = 2\beta^2 \kappa g(y_i) [DU(y_i) - D\bar{\varepsilon}_n],
\]

With the substitutions of \( DU(y_i) \) and the Morse potential given in equation (4), the effective potential then looks like

\[
V_{eff} = 2\beta^2 \kappa g(y_i) [D(e^{-\alpha y} - 1)^2 + \frac{1}{2\beta} \ln[g(y)] - D\bar{\varepsilon}_n].
\]

where \( g(y) \) is defined in equation (4). Notice that equation (16) is an eigenfunction equation where the eigenvalue is zero and the effective potential depends of the original energy eigenvalue of the initial problem, \( \bar{\varepsilon}_n \), and the temperature. To apply the variational method at any fixed temperature, we have firstly to choose a trial wave function that depends on the variational parameter \( \mu \) and that minimizes the energy \( \bar{\varepsilon}_n \), an satisfies (13).

The parameters used in the effective potential (18) were the same as found in reference [15], in which the thermodynamic properties of the PBD model were calculated using numerical methods, i.e., \( \rho = 1, \alpha = 0.35 \text{Å}^{-1}, \kappa = 0.06 \text{eV} \text{Å}^{-2}, a = 4.5 \text{Å}^{-1} \) and \( D = 0.03 \text{eV} \).

To choose the trial function for the lowest level it is necessary to know the general characteristics of the effective potential. The starting point is the Morse potential, Fig. 1 presents in the same graph, for comparison, the plots of the effective potential \( V_{eff} \) (with parameters: \( \rho = 1, \alpha = 0.35 \text{Å}^{-1}, \kappa = 0.06 \text{eV} \text{Å}^{-2}, a = 4.5 \text{Å}^{-1}, D = 0.03 \text{eV}, T = 200 \text{K} \) and \( \bar{\varepsilon}_n = 0.0260309 \text{eV} \) and the shifted Morse potential, \( V_M(y) = D_M(e^{-2a_M y} - 2e^{-a_M y}) - c \), (with parameters \( D_M = 0.053 \text{eV} \) and \( a_M = 3.6 \text{Å}^{-1}, c = 0.03 \)).

Considering the similarity between the effective potential and the Morse potential, especially in the vicinity of the wells with similar depths, which is the most important region in the phase transition study, the trial function chosen for the variational method is the ground state Morse potential solution with the parameters such that both potentials become as close as possible. Thus, the trial function used is given by ground state solution of Morse potential, [33],

\[
\Psi_{0\mu} \propto e^{-d e^{-\mu y}} e^{-(d-\frac{1}{2})\mu y}
\]

where \( d \equiv (\frac{2}{\pi})^2(2\kappa D)^{1/2} > \frac{1}{2} \) and \( \mu \) is the variational parameter.

Once the trial function (19) is chosen, the adapted variational method is applied by varying the energy \( \bar{\varepsilon}_n \). The integration (13) and the minimization with respect to the parameter
µ are made to find the mean value of the effective Hamiltonian (11) until it is numerically equal to the fixed constant zero. When this occurs the value of \( \bar{\varepsilon}_n \) is the value of energy of the original problem. Moreover, once the variational parameter is fixed by the minimization process, the wave function is fixed and it is used to calculate the mean stretching \( <y> \), defined in (6). This procedure is repeated for different values of the temperature. Fig. 2 shows that for temperatures around 340K, the mean stretching increases significantly, indicating that the phase transition occurs in the chain. This temperature coincides with the one expected for the thermal denaturation of the DNA molecule found in reference [31].

5. Conclusions
The main point of this paper is to present an analytic method, the adapted variational method to solve a second order equation that resembles a Schrödinger equation with position-dependent mass. The methodology applied in the evaluation of the mean stretching of the DNA molecule showed that a phase transition occurs for a temperature consistent with that found in the literature [31] for this macromolecule.

The variational method, although it is commonly used in the context of quantum mechanics to study the Schrödinger equation, has not yet been applied to solve problems with position-dependent mass.

It is important to remark that the adopted approach is a good analytic alternative but it is a technique of quantum physics used to solve a statistical problem.
From the results obtained, it is possible to conclude that the adopted approach is a good alternative to study this type of problem with position-dependent mass.

We conclude that the new methodology provides a useful mathematical tool to analyse the thermodynamic properties of the PBD model for the DNA. The approach introduced here is general and can be extended for other models with different potentials simulating the stacking and/or the H-bond interactions.

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6. References
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