

DNA denaturation as a problem of translational-symmetry restoration

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We study the quantum-mechanical version of a model proposed by Peyrard and Bishop [Phys. Rev. Lett. **62**, 2755 (1989)] to describe the denaturation phenomenon on the DNA double helix. We characterize denaturation as a phase transition leading to the restoration of the translational invariance of the system. The problem is approached via a modified perturbative theory which incorporates also nonperturbative effects. These are accounted by an auxiliary random variable u describing the equilibrium positions of the constituting particles. The criticality of the model is revealed by analyzing equations involving the first and second cumulants of the u -distribution function. As a consequence, an analytical expression for the critical temperature T_c is obtained as a function of all model parameters.

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I. INTRODUCTION

Physical models describing the DNA molecule as a statistical-mechanics system of interacting particles (atoms and/or molecules) have been proposed and analyzed in order to characterize the nature of the melting of its hydrogen bonds [1,2]. These H bonds connect each nucleotide in one of the two strands of the DNA helix to its "complementary" nucleotide on the other strand. Experiments indicate that this transition, also known as "DNA denaturation," occurs at temperatures ranging between 350 and 400 K depending on the specific sequence of nucleotides that compose the molecule [3].

An extensive study has been carried out by Prohovsky and collaborators [1] based on a self-consistent phonon approximation to treat some realistic models with Morse-like potentials modeling the H bonds. Their analysis indicates that a certain correlation function presents an instability at a finite temperature T_c , which is identified as the critical temperature for melting.

More recently, Peyrard and Bishop [2] presented a simplified model to describe the DNA molecule where irrelevant degrees of freedom for purposes of studying the phenomenon of denaturation are *a priori* eliminated. In this model, harmonic interactions are considered between particles on the same strand while the H bonds are also modeled by Morse potentials. Each of these particles represents a nucleotide. The classical statistical mechanism of the model has been explicitly solved by the authors using the transfer-matrix technique. Also in this case there are strong indications that the corresponding correlation function loses stability as the temperature approaches T_c .

Here we address the quantum-statistical-mechanics version of the Peyrard-Bishop model. Our motivation in studying the quantum model is to investigate the role played by the mass M of the nucleotides on the denaturation process. Since the kinetic and the potential terms of the Hamiltonian quantum model do not commute with each other we shall expect that M is an important parameter in the melting dynamics. This should be contrasted

with the classical model where the kinetic energy cancels out against the normalization in the expression for the correlation of interest. Because of this, the two versions of the model should be distinguished.

To treat the problem, we focus on an important feature of the Morse potential: it is a bounded asymmetric potential with a finite number of bound states. From this, we can argue that (i) for $T < T_c$ the system necessarily presents itself in a state which is not invariant with respect to translations along the direction of the H bonds, and (ii) the asymmetry produces a shift on the equilibrium positions of the constituting particles. With regard to these, our treatment is not restricted to the Morse potential since any other potential presenting these properties and satisfying the same physical-chemical requirements could be equally considered. We choose the same potential as in Ref. [2] in order to compare the classical and quantum results.

In the limit of $N \rightarrow \infty$, N being the total number of particle pairs, we characterize the denaturation process as a phase transition leading to a restoration of the translational invariance of the system along the direction of the H bonds. In the present case it corresponds to a situation of two mutually noninteracting chains of harmonic oscillators. When applied to the expression for G , the Green's function of interest, the symmetry restoration requirement leads to an analytical expression for T_c as a function of all model parameters. When compared to the classical results, the presence of M in this expression leads to a dramatic change in fixing the remaining parameters to fit T_c on experimental values.

The calculation of G is accomplished here through a modified perturbative theory in which we distinguish two regions of momentum integration whose associated processes (in terms of phonon interactions) play quite different roles in the melting transition. The region of high momentum transfer is treated perturbatively since it corresponds to small displacements of the particles (nucleotides) from their equilibrium positions. On the other hand, the region of low momentum transfer, which is characterized by processes involving large displacements

of the particles, cannot, in principle, be accounted for by a perturbative approach. Near the critical temperature large displacements are in fact important and their contributions to the dynamics of the system cannot be neglected.

Qualitatively, the main difference between the contributions from these two regions lies in the fact that a particle in thermal equilibrium subjected to "large" displacements under a Morse potential (or any other presenting a certain degree of anharmonicity) effectively changes its equilibrium position with variations of temperature [4]. Because (as we assume here) during the denaturation the neighboring nucleotides in the same strand remain connected by harmonic forces, the change on the equilibrium position of each of these particles along the direction of H bonds leads to a corresponding shift of the whole strand relatively to its initial position (at $T=0$). For small displacements of the particles, this effect is negligible.

This suggests that we account for the contributions to the melting from both regions of momentum transfer by Fourier analyzing the displacement y_j of the particle pair j along the direction of the H bonds with respect to its initial equilibrium position R_j as $y_j = u + (1/\sqrt{N}) \sum_k v_k e^{ikR_j/b}$ (See Sec. II for details). With this, the low-momentum-transfer processes are accounted by the *random* variable u which describes explicitly the shift on the equilibrium position of the whole chain. Accordingly, these nonperturbative processes are incorporated into the perturbative series for G by parameterizing them through the expectation values $\langle u \rangle$ and $\langle uu \rangle^c$, the first and second cumulants, respectively, of the u -distribution function, which is, in principle, unknown. We should mention that this procedure resembles Wilson's operator product expansion [5(a)] as applied to quantum chromodynamics [5(b)].

Quantitatively, the distinction between high and low momenta in the course of the G calculation is done by introducing a scale ω_0 into the theory that restrains integration over low momentum in the perturbative region, so that it becomes infrared divergent free. We estimate this scale by a variational method suggested by Feynman [4].

An expression for G is obtained by resumming an infinite number of Feynman's diagrams belonging to certain classes. These diagrams representing the terms of the modified perturbative series proposed above are accompanied by corresponding factors of $\langle u \rangle$ and $\langle uu \rangle^c$. A subsequent use of Dyson's equation allow us to write G as $G \simeq [(M\beta)(\omega_k^2 + \mu_p^2 + \Delta)]^{-1}$ in the momentum representation. For $\Delta=0$ it coincides with G_0 , the free-phonon Green's function. It follows that a natural characterization of the melting transition comes from the condition $\Delta=0$ at $T=T_c$. The "gap" Δ is a function of all model parameters; besides, it is also a function of $\langle u \rangle$, $\langle uu \rangle^c$, and $\beta=1/k_B T$. The critical temperature T_c and $\langle u \rangle$ at $T=T_c$, i.e., $\langle u \rangle_{T_c}$, are determined by solving the following equations at the critical point: (a) a self-consistent equation (SCE) established for Δ by considering all self-similar insertions into the diagrams mentioned above and

(b) an equation derived from the minimization of the total free energy F of the system with respect to $\langle u \rangle$: $(\partial F/\partial \langle u \rangle)=0$. Additional physical considerations require that $\langle uu \rangle^c=0$ at T_c .

In Sec. II we present the model of Ref. [2] and outline the modified perturbative approach proposed here. The SCE for Δ , the total free energy of the system, and the final expression for T_c are derived in Sec. III. We discuss our results in Sec. IV.

II. OUTLINES

A. Model

The model Hamiltonian proposed by Peyrard and Bishop [2] describing the DNA molecule is given by (we use the same notation as in [2])

$$H = \sum_{n=1}^N \left\{ \frac{1}{2} M (\dot{u}_n^2 + \dot{v}_n^2) + \frac{1}{2} K [(u_n - u_{n-1})^2 + (v_n - v_{n-1})^2] + V(u_n - v_n) \right\} \quad (1)$$

where

$$V(u_n - v_n) = D \{ \exp[-a(u_n - v_n)] - 1 \}^2 \quad (2)$$

is the Morse potential describing the H bonds that connect the complementary nucleotides in pairs.

In (1), u_n is the displacement of the particle n from its equilibrium position in one of the two strands and v_n is the corresponding variable for the complementary particle on the other strand. Both u_n and v_n describe the movements of the particles along the direction of the H bonds. As noted by the authors, it is not necessary to consider other polarizations in modeling the DNA in order to study the denaturation phenomenon, for they would be factorized and subsequently canceled out by renormalization in calculating averages of the variables u_n and v_n . A common mass M and spring constant K are used for all particles (nucleotides).

As also noted in [2], by defining $x_n = (u_n + v_n)/\sqrt{2}$ and $y_n = (u_n - v_n)/\sqrt{2}$, the Hamiltonian (1) is decoupled as $H = H_0(x) + H(y)$, where

$$H(y) = H_0(y) + V(y), \quad (3)$$

$$H_0(y) = \sum_n \left\{ \frac{p_n^2}{2M} + \frac{1}{2} K (y_n - y_{n-1})^2 \right\}, \quad p_n = M \dot{y}_n, \quad (4)$$

$$V(y) = D \sum_n \{ \exp[-a\sqrt{2}y_n] - 1 \}^2. \quad (5a)$$

It shall be convenient for what following to write V as a series expansion:

$$V(y) = D \sum_n \sum_{p=2}^{\infty} \frac{(-1)^p}{p!} [(2\sqrt{2}ay_n)^p - 2(\sqrt{2}ay_n)^p]. \quad (5b)$$

$H_0(x)$ and $H(y)$ describe, respectively, the in-phase and out-of-phase relative displacements for the pair of particles from their equilibrium positions. For the purpose of studying the melting of the H bonds, $H_0(x)$ is ir-

relevant. Accordingly, there is no loss of generality in restricting the analysis to the chain described by $H(y)$.

B. Modified perturbative theory

As mentioned above, the effective shift of the relative equilibrium position of the strand is considered here through the introduction of an auxiliary temperature-dependent *random* variable u modifying the standard Fourier transformation for the variables y_n 's as

$$y_n(\sigma) - u \equiv \bar{y}_n(\sigma) = \frac{1}{\sqrt{N}} \sum_k e^{ikR_n/b} v_k(\sigma) \quad (6)$$

where $\sigma = it$ has dimension of $\beta = 1/k_B T$; k_B is the Boltzmann constant, and T is the temperature of the system. N is the total number of nucleotides on the strand, b is the lattice constant, and $k = \pi l/N$, $l = -N, -N+1, \dots, 0, \dots, N$, assuming periodical boundary conditions. R_n is the equilibrium position of the n th particle on the strand.

Note that, although the modes with $k \neq 0$ are not modified by the introduction of u in (6), the zero mode obeys

$$v_0 = \frac{1}{\sqrt{N}} \sum_n y_n - \sqrt{N} u. \quad (7)$$

From this, we shall assume that all v_k 's, including $k=0$, account for symmetric fluctuations of the chain around its equilibrium position stated by u .

According to the second quantization formalism, the normal modes v_k are written in terms of creation b_k^\dagger and annihilation b_k operators for free phonons [6]:

$$v_k(\sigma) = \frac{1}{(2M\omega_k)^{1/2}} [b_k^\dagger(\sigma) + b_k(\sigma)], \quad (8)$$

$$\omega_k = \left[\frac{2K}{M} (1 - \cos k) \right]^{1/2}. \quad (9)$$

In (9), \hbar and the lattice constant were set equal to the unity. Using (6) and (8), and apart from terms involving \dot{u} which in principle can be incorporated to $V(y)$, the free Hamiltonian H_0 in (4) becomes

$$H_0 = \sum_k \omega_k (b_k^\dagger b_k + \frac{1}{2}). \quad (10)$$

The quantity to be examined here in order to obtain information on the melting transition is the temperature Green's function defined by

$$G_{ij}(\sigma) = \langle \mathcal{T}[\bar{y}_i(\sigma)\bar{y}_j(0)] \rangle \quad (11)$$

where \mathcal{T} is the "time"-ordering operator and

$$\langle \mathcal{O} \rangle \equiv \frac{\text{Tr}\{e^{-\beta H} \mathcal{O}\}}{\text{Tr}\{e^{-\beta H}\}}$$

is the thermal average of the operator \mathcal{O} .

A measure of the fluctuations on the characteristic distance between the originally paired particles is given by

$$\lim_{\sigma \rightarrow 0} G_{ii}(\sigma). \quad (12)$$

The standard perturbative expansion for $G_{ij}(\sigma)$ is written as [6,7]

$$G_{ij} = \langle \mathcal{T}[\bar{y}_i(\sigma)\bar{y}_j(0)] \rangle_0 - \left\langle \mathcal{T} \left[\int_0^\beta \bar{V}(\sigma_1)\bar{y}_i(\sigma)\bar{y}_j(0) d\sigma_1 \right] \right\rangle_0 + \frac{1}{2!} \left\langle \mathcal{T} \left[\int_0^\beta d\sigma_1 \int_0^\beta d\sigma_2 \bar{V}(\sigma_1)\bar{V}(\sigma_2)\bar{y}_i(\sigma)\bar{y}_j(0) \right] \right\rangle_0 + \dots \quad (13)$$

The thermal averages above are defined by $\langle \mathcal{O} \rangle_0 \equiv \text{Tr}[\exp(-\beta H_0)\mathcal{O}]/\text{Tr}[\exp(-\beta H_0)]$ for H_0 as in (10). \bar{V} is a generic perturbation. The first term on the right-hand side (rhs) of (13) is the free-phonon-temperature Green's function [6]

$$\langle \mathcal{T}[\bar{y}_i(\sigma)\bar{y}_j(0)] \rangle_0 \equiv G_{ij}^{(0)}(\sigma) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} dk e^{ik(R_i - R_j)} \sum_p e^{i\mu_p \sigma} G_k^{(0)}(\mu_p).$$

In replacing the sum by the integral over k in the expression above, the limit $N \rightarrow \infty$ was taken. $\mu_p = 2\pi p/\beta$ for $p = 0, \pm 1, \pm 2, \dots$ are the Matsubara's frequencies and

$$G_k^{(0)}(\mu_p) = \frac{1}{(M\beta)(\mu_p^2 + \omega_k^2)}. \quad (14)$$

For considering other terms in (13), some remarks are in order. Because the free part of the theory whose dynamics is set by H_0 presents an infrared divergence, it does not allow for perturbations from processes involving low momentum transfer. Consequently, in choosing V [expression (5b)] as \bar{V} in (13), we should select from the whole set of processes contained in each term in this series only those involving high momentum transfer. Instead, in order to account also for the nonperturbative processes, we modify expression (13) as follows:

$$G_{ij} = \langle \langle \mathcal{T}[\bar{y}_i(\sigma)\bar{y}_j(0)] \rangle \rangle - \left\langle \left\langle \mathcal{T} \left[\int_0^\beta V(\sigma_1)\bar{y}_i(\sigma)\bar{y}_j(0) d\sigma_1 \right] \right\rangle \right\rangle + \frac{1}{2!} \left\langle \left\langle \mathcal{T} \left[\int_0^\beta d\sigma_1 \int_0^\beta d\sigma_2 V(\sigma_1)V(\sigma_2)\bar{y}_i(\sigma)\bar{y}_j(0) \right] \right\rangle \right\rangle + \dots \quad (13')$$

The thermal averages indicated above are defined by

$$\langle\langle \rangle\rangle \equiv \langle\langle \rangle_{(u)} \rangle_0^{[\omega_0]}$$

where $\langle \rangle_{(u)}$ acts only on the nonperturbative part taking thermal averages of products of operators u calculated with the u -distribution function while $\langle \rangle_0^{[\omega_0]}$ acts only on the perturbative part taking thermal averages of operators v_k calculated with (10) and subjected to the infrared cutoff ω_0 , which shall be introduced into the theory to restrain integration over low momentum in this region.

Besides, as long as the anharmonicities exhibited by the Morse potential do not play an important role in the region of high momentum, we believe that it is sufficient to consider for the perturbative part only processes originated from the quadratic and quartic terms in v_k . Moreover, we restrict our calculation in this region up to the second term in (13'). In terms of Feynman's diagrams, these perturbative processes can be represented by the "skeleton diagrams" as in Fig. 1.

Contributions from the processes involving low momentum transfer are accounted for through the variable u ; for this region all (infinite) terms on the rhs of expression (5b) are equally considered in the calculation. To be more precise, each term in (5b) is Fourier analyzed according to (6). This provides a set of terms containing products of v_k 's and u 's. From these, we keep only those containing quadratic and quartic terms in v_k , the remaining factors being of the u component. For the perturbative part in each of these selected terms, i.e., for the factors in v_k , the thermal averages are taken using (10). For the nonperturbative part, i.e., for the products in u , thermal averages should in principle be taken using the u -distribution function. However, because we are not able to determine this function here, we approximate each of these u averages by its cumulant expansion up to first $\langle u \rangle$ and second $\langle uu \rangle^c$ cumulants:

$$\langle u^m \rangle_{(u)} \simeq m! \sum_{m_1, m_2} \frac{1}{m_1!} \left[\frac{\langle u \rangle}{1!} \right]^{m_1} \frac{1}{m_2!} \left[\frac{\langle uu \rangle^c}{2!} \right]^{m_2} \times \delta_{m_1 + 2m_2, m} \quad (15)$$

where m, m_1 , and m_2 are integers.

Subsequently we let $\langle u \rangle$ and $\langle uu \rangle^c$ act as T -dependent parameters of the theory. At the critical point, $\langle u \rangle$ is obtained through the minimization of F , the total free-energy of the system (which can be obtained

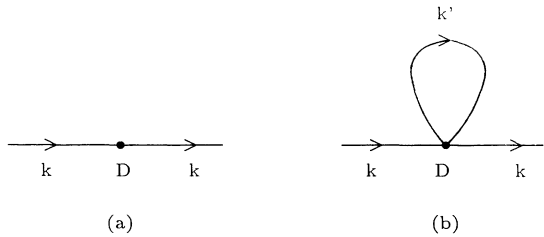


FIG. 1. Skeleton diagrams representing perturbative processes (first order in the parameter D). (a) Quadratic terms in v_k ; (b) quartic terms in v_k .

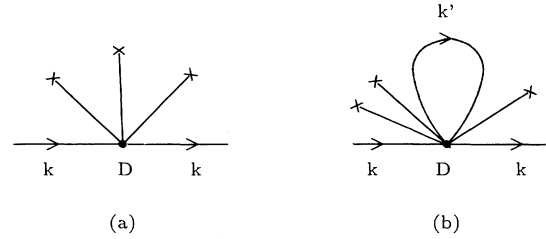


FIG. 2. Skeleton diagrams modified by the nonperturbative processes— \times signals the presence of a u operator.

through G), with respect to this parameter: $(\partial F / \partial \langle u \rangle)_{T=T_c} = 0$. Since nonperturbative processes take place only for $T < T_c$, the random variable u shall assume a definite value at the critical point. This set the condition $\langle uu \rangle^c = 0$ at $T = T_c$.

From this whole procedure, the second term on the rhs of (13') can be represented as a sum over infinite diagrams, all of them determined by the same (perturbative) skeletons. They differ from each other by the corresponding "insertions" of $\langle u \rangle$ and $\langle uu \rangle^c$. Examples of these "modified diagrams" are in Fig. 2.

Because the perturbative part is the same for all of these diagrams, it factorizes for each skeleton case. We are then able to recuperate in a certain sense the specific features of the Morse potential through the nonperturbative part of the problem by summing up all of the above-mentioned diagrams. This calculation involves a combinatorial computation to account for all factors of $\langle u \rangle$ and $\langle uu \rangle^c$ derived from (15) for each diagram. The final expression for the second term on the rhs of (13') is then expressed as a sum over two terms: one relative to the skeleton represented in Fig. 1(a) and the other to the one in Fig. 1(b).

Next, we show in more detail how these ideas work and obtain the final expression for G . This expression in turn reveals very clearly the conditions for melting. From the analysis of these conditions which involve the limiting values for $\langle u \rangle$ and $\langle uu \rangle^c$ at the critical point, we obtain T_c .

III. GREEN'S-FUNCTION CALCULATION AND THE MELTING TRANSITION CHARACTERIZATION

According to the proposal above, the Morse potential V is expanded in powers of the displacements y_n as in (5b). With this, the second term on the rhs of (13') can be written as

$$G_{ij}^{(1)}(\sigma) = -D \int_0^{a\sqrt{2}} d\alpha \int_0^{a\sqrt{2}} d\gamma \sum_{q=0}^{\infty} G_{ij}^q(\sigma), \quad (16)$$

$$G_{ij}^q(\sigma) = \sum_n \int_0^\beta d\sigma_1 \frac{1}{q!} [-(\alpha + \gamma)]^q \times \langle\langle y_n^{q+2}(\sigma_1) \bar{y}_i(\sigma) \bar{y}_j(0) \rangle\rangle, \quad (17)$$

where α and γ are auxiliary variables introduced here to

facilitate the resummation of the terms in (16).

All of the y 's in (17) should now be Fourier analyzed as in (6). For practical purposes, however, in order to select the terms in (17) containing quadratic factors in v_k we proceed with the computation by counting all possibilities of selecting two distinct operators y_n from the total of $(2+q)y_n$'s and write them in the phonon representation. Along with \bar{y}_i and \bar{y}_j (also in terms of b_k and b_k^\dagger), these selected operators give rise to the external legs of the corresponding diagrams. For the remaining qy_n 's we take only the u component. After approximating the

thermal averages of the u products by their cumulant expansions as in (15), and performing the sum over q (which involves a quite extensive combinatorial computation) and the integrals over α and γ indicated in (16), we obtain

$$G_{ij}^{[1,2]}(\sigma) \cong S[G_{ij}^{(0)}(\sigma)]^2 \quad (18)$$

where the first superscript in G indicates as before the order of the term in (13) and the second corresponds to the number of factors v_k .

$$S = 4a^2 [(2e^{4a^2\langle uu \rangle^c} - e^{a^2\langle uu \rangle^c}) + (2e^{-2\sqrt{2}a\langle u \rangle} - e^{-\sqrt{2}a\langle u \rangle} - 1)] + \tilde{S}, \quad (19)$$

$$\begin{aligned} \tilde{S} = 4a^2 & \left[\frac{2\langle u \rangle}{\sqrt{\langle uu \rangle^c}} \operatorname{erfc}[z] \exp \left[4a^2\langle uu \rangle^c + \frac{\langle u \rangle^2}{2\langle uu \rangle^c} \right] - \sqrt{2}e^{-2\sqrt{2}a\langle u \rangle} \right] \\ & + 4a^2 \left[-\frac{1}{2\sqrt{2}} \frac{\langle u \rangle}{\sqrt{\langle uu \rangle^c}} \operatorname{erfc}[z/2] \exp \left[2a^2\langle uu \rangle^c + \frac{\langle u \rangle^2}{4\langle uu \rangle^c} \right] + \frac{1}{2\sqrt{2}} e^{-\sqrt{2}a\langle u \rangle} \right] \end{aligned} \quad (20)$$

where

$$\operatorname{erfc}[z] = \int_z^\infty dp e^{-p^2}$$

and

$$z = 2a\sqrt{\langle uu \rangle^c} + \frac{\langle u \rangle}{2\sqrt{\langle uu \rangle^c}}. \quad (21)$$

For the quartic terms in the perturbative part, four y_n 's should be initially selected among the total of $(2+q)y_n$'s. In this case, we obtain the result

$$G_{ij}^{[1,4]} \cong S_L [G_{ij}^{(0)}(\sigma)]^2 \mathcal{L} \quad (22)$$

where

$$S_L = \frac{4a^2}{\langle uu \rangle^c} [2e^{4a^2\langle uu \rangle^c} - e^{a^2\langle uu \rangle^c} - 1] + \frac{\tilde{S}}{\langle uu \rangle^c}. \quad (23)$$

In (22) \mathcal{L} expresses the contribution from the integration over the internal loop momentum of Fig. 1(b). Using the expressions above we write G in the momentum representation, up to first order in the parameter D , as

$$\tilde{G}_k(\mu_p) \cong G_k^{(0)}(\mu_p) - \beta D(S + S_L \mathcal{L}) [G_k^{(0)}(\mu_p)]^2. \quad (24)$$

The use of Dyson's equation now allows us to write the final expression for G as

$$G_k(\mu_p) \cong \frac{1}{M\beta(\mu_p^2 + \omega_k^2 + \Delta)} \quad (25)$$

where the gap function Δ is defined by

$$\Delta = \frac{D}{M}(S + S_L \mathcal{L}). \quad (26)$$

Conclusions on the melting transition are obtained here by analyzing Δ . First, we note that a SCE for this quantity can be established by replacing the free-phonon

propagator occurring in the loop by the "dressed propagator" (25). In fact, with this substitution and after summing over the Matsubara's frequencies, the loop factor \mathcal{L} becomes

$$\mathcal{L}(\Delta, \beta) + \frac{1}{2\pi M} \int' dk \frac{1}{2\Omega_k} \coth(\beta\Omega_k/2) \quad (27)$$

where

$$\Omega_k = [(2K/M)(1 - \cos k) + \Delta]^{1/2}. \quad (28)$$

The prime to the integral symbol indicates that integration over low momentum should be avoided. We approximate (27) by

$$\mathcal{L}(\Delta, \beta) \approx \frac{1}{\pi\beta M} \int_{\omega_0^2}^{4K/M} \frac{dx}{(x + \Delta)[(4K/M)x - x^2]^{1/2}}. \quad (29)$$

The expression above is obtained from (27) by approximating $\coth(\beta\Omega_k/2)$ by $(\beta\Omega_k/2)^{-1}$ and by changing the variable of integration. Moreover, we introduce a cutoff ω_0 for the frequencies. (26) and (29) define the SCE for Δ .

At $T = T_c$ we expect that the two original chains of harmonic oscillators decouple from each other meaning that G should coincide with $G^{(0)}$ at the critical point. In view of the form of G in (25), the condition that establishes the melting transition is

$$\Delta = 0 \quad \text{at } T = T_c, \quad (30)$$

which corresponds to a translational invariant state of the system (note that the free Hamiltonian H_0 is invariant under the transformation: $y_i \rightarrow y_i + \xi$ where ξ is a time-independent parameter).

We shall then look for solutions for T_c in the SCE for $\Delta = 0$. This also requires the values for ω_0 , $\langle u \rangle$ and

$\langle uu \rangle^c$ at the critical point. We had already mentioned that $\langle uu \rangle^c = 0$ at $T = T_c$. The other two parameters will be fixed as follows.

(i) ω_0 . In order to estimate ω_0 we focus on the "zero-mode" movement (i.e., the displacements of the chain as a whole from its equilibrium position) neglecting for a while its interaction with the fast modes. As explained before, this is equivalent of studying the movements of just a single particle under a Morse potential (5). The solution to this problem presents a finite number of bounded states [8]. On the other hand, as suggested by Feynman [4], for a system in thermal equilibrium subjected to any bounded potential $V(z)$, a suitable replacement

$$H = \frac{p^2}{2M} + V(z) \rightarrow H_0 = \frac{p^2}{2M} + \frac{M\omega^2}{2}(z - \langle z \rangle)^2 \quad (31)$$

is possible since the (temperature-dependent) parameters ω and $\langle z \rangle$ are obtained from (a) $\langle V'(z) \rangle_0 = 0$, ensuring that the force acting on the particle vanishes at the equilibrium position; and (b) $\langle zV'(z) \rangle_0 = \langle p^2/M \rangle_0$, by the Virial's theorem. These conditions provide the best quadratic approximation for the original Hamiltonian. If we take $V(z)$ as the Morse potential (5a), equations (a) and (b) provide

$$\omega \simeq \left[\frac{M\beta}{2a^2q} \right]^{-1/2}, \quad (32a)$$

$$e^{2q} \simeq 8(aD)^2\beta^3/M \quad (32b)$$

for $\beta\omega/2 \ll 1$. Here $q \equiv (2\sqrt{2}/3)a\langle z \rangle$.

We estimate ω_0 as the minimum value for ω , i.e., ω_{\min} , for which a solution to the Eqs. (32a) and (32b) exists:

$$\omega_0 = \omega_{\min} \simeq (32a^4D/\sqrt{e}M^2)^{1/3} \quad (33)$$

for

$$\langle \bar{z} \rangle \simeq 3\sqrt{2}/8a, \quad \bar{\beta} \simeq [(2aD)^2/eM]^{-1/3}. \quad (34)$$

We note that (33) and (34) are limiting values for the corresponding parameters for which the particle remains bounded.

Using result (33) and taking $\Delta = 0$ in (29), we obtain

$$\mathcal{L} \simeq \frac{1}{2\pi\beta K} \sqrt{R-1} \quad (35)$$

with

$$R \equiv (4K/M)/\omega_0^2. \quad (36)$$

(ii) $\langle u \rangle$ at $T = T_c$. We estimate $\langle u \rangle$ at the critical point, i.e., $\langle u \rangle_{T_c}$ by minimizing the total free energy F of the system described by $H(y)$ with respect to this parameter. F can be calculated using the Green's function (25) through [6]

$$F = F_0 + \lim_{\sigma \rightarrow 0^+} \frac{M}{2} \int_0^1 \frac{d\lambda}{\lambda} \int dk \sum_p (\lambda\Delta) G_k(\lambda, \mu_p) e^{i\mu_p \sigma}$$

for

$$G_k(\lambda, \mu_p) = \frac{1}{M\beta(\mu_p^2 + \omega_k^2 + \lambda\Delta)}.$$

It results in

$$F = \frac{1}{\beta} \int dk \ln \sinh(\beta\Omega_k/2). \quad (37)$$

We take

$$\frac{\partial F}{\partial \langle u \rangle} = 0 \quad \text{at } T = T_c. \quad (38)$$

Using the SCE (26), Eq. (38) can be written as

$$\frac{\partial S}{\partial \langle u \rangle} + \mathcal{L} \frac{\partial S_L}{\partial \langle u \rangle} = 0. \quad (39)$$

We use expressions (19) and (23) for S and S_L , respectively, to calculate the derivatives above at the critical point, i.e., we set $\Delta = 0$ and take the limit for $\langle uu \rangle^c \rightarrow 0$. It follows from (39) that

$$t_c(4t_c - 1) \left[\frac{2}{\pi \langle u \rangle_{T_c}^2} \mathcal{L}(\Delta = 0, \beta_c) - \sqrt{2} \right] = 0 \quad (40)$$

with

$$t_c \equiv \exp(-\sqrt{2}a\langle u \rangle_{T_c}).$$

As a physical solution for the above equation, we choose

$$t_c = \frac{1}{4}, \quad (41)$$

which implies that $\langle u \rangle_{T_c} \simeq a^{-1}$.

Introducing this value for $\langle u \rangle_{T_c}$ into the SCE for $\Delta = 0$ and taking again the limit $\langle uu \rangle^c \rightarrow 0$, we obtain the following expression for T_c :

$$T_c \simeq \frac{1}{k_B} \left[\frac{\pi K}{28a^2} \right] \frac{1}{\sqrt{R-1}}. \quad (42)$$

IV. DISCUSSION

Analyzing the expression obtained for $G_k(\mu_p)$, Eq. (25), the denaturation phenomenon could be characterized here (in the limit $N \rightarrow \infty$) as a phase transition leading to the restoration of the translational invariance of the system. In fact, the condition $\Delta = 0$, shown to be satisfied at a finite temperature T_c , allows for the possibility for the chain described by $H(y)$ to execute arbitrary large displacements along the direction of the H bonds. This possibility is manifested through a divergent behavior of the mean quadratic deviation:

$$\langle \bar{y}_i^2 \rangle = G_{ii} = \left[\int_{-\pi}^{\pi} dk \sum_p G_k(\mu_p) e^{ik(R_i - R_j)} \right]_{i=j}. \quad (43)$$

For any $\Delta \neq 0$ the integral above gives a finite value for $\langle \bar{y}_i^2 \rangle$. For $\Delta = 0$, however, this quantity presents an infrared divergence. The very fact that we could obtain a finite solution for T_c for $\Delta = 0$ supports some experimental results suggesting that the DNA helix melting occurs as a sharp transition [9]. The passage from $\Delta \neq 0$ to $\Delta = 0$ indicates the occurrence of a transition from a bound state of the strain to a free state. For a complete study of the transition, however, an analysis of the stability of the

solution $\Delta=0$ to the SCE (26) would be desirable.

It is important at this point to call attention to the hypotheses involved in our approach. (i) We assume that the fast modes can be distinguished from the slow modes defining in this way two distinct regions of phonon momenta. (ii) In the perturbative region, we approximate the Morse potential by a few terms of its expansion in powers of the displacements (only the terms in \bar{y}_n^2 and \bar{y}_n^4 are considered). In this approximation, we neglect, for instance, phonon decay processes. (iii) Although in the nonperturbative region all powers of the above series are considered in the calculation, only the first and second cumulants are taken for approximating average of powers of the variable u . (iv) Finally, motivated by the necessity of defining quantitatively the separation between the two regions of momenta, we introduce a scale ω_0 , which we assume can be determined by focusing on the slow modes alone.

The first three hypotheses seem quite reasonable within the context of the problem studied. The fourth one involves necessarily an *external* input to the model since it does not provide us with a natural scale. The fact that we are able to establish here such a scale by choosing one particular (external) criterion does not rule out other possibilities. We should note, however, that, since ω_0 sets up dependences of T_c on parameters of the model, one can check the reliability of this particular choice on experimental grounds. For example, it would be interesting to investigate specifically the dependence of T_c on the mass parameter M . Here we obtain that $T_c \sim M^{-1/6}$ for $R \gg 1$. For the other parameters, the dependence shown in expression (42) is as one should expect from simple physical considerations. Concerning M it is interesting to observe that since for a *classical* system $[\bar{y}_n, \bar{y}_n] = 0$, one should not expect in this case that results for $\langle \bar{y}_i^2 \rangle$ would carry a dependence on M because in calculating this average, the kinetic term cancels out against the normalization factor. For the quantum case this does not happen, of course. From a physical point of view, we do expect that the masses of the particles involved play some role in the transition which in turn should be expressed through T_c .

All nonperturbative contributions are expressed through S and S_L . Their functional dependences on $\langle u \rangle$ and $\langle uu \rangle^c$ reflect the particular way by which, in the context of this model, the fast modes interact with the slow modes in the process of melting. A remark is in order here: had we set $\langle uu \rangle^c = 0$ since the beginning of the calculation, instead of taking the limit $\langle uu \rangle^c \rightarrow 0$ at $T = T_c$, we would not have obtained a meaningful result for T_c in the limit of $N \rightarrow \infty$. This fact expresses the necessity of considering at least two parameters for representing the nonperturbative contributions in this

case. The shift on the equilibrium positions can only be accomplished by high-order phonon processes occurring in the nonperturbative region. Because these have an intrinsic statistical character it explains the necessity of considering u as a *random* variable. Hence, before the transition takes place, $\langle uu \rangle^c \neq 0$.

Finally, we analyze the possibility for obtaining a numerical value for T_c from expression (42) compatible with the experimental range of values for melting temperature in the DNA molecule [3]. We use the same values for the parameters of the Morse potential as suggested in Ref. [2]: $a = 1.8 \text{ \AA}^{-1}$ and $D = 0.33 \text{ eV}$. For M , we choose $M = 3.0 \times 10^{11} \text{ eV}$ ($\approx 325 \text{ amu}$). We vary the spring constant K within the range of values allowed by the condition $R > 1$ (i.e., $K > M\omega_0^2/4$). This is a necessary condition for the existence of a perturbative region in which integral (29) is performed. We found that for $K \approx 10 \text{ eV \AA}^{-2}$ the critical temperature approaches to the experimental values. This value for K should be compared with the result obtained in Ref. [2] for the classical case; there, $K \approx 3 \times 10^{-3} \text{ eV \AA}^{-2}$. Recently, another set of values for the model parameters were suggested in Ref. [10] including that for the spring constant: $K = 0.06 \text{ eV \AA}^{-2}$, $D = 0.04 \text{ eV}$, and $a = 4.45 \text{ \AA}^{-1}$. Unfortunately, they do not satisfy the condition above: with a and D we use expression (33) to calculate $\omega_0^2 \approx 10^{-5} \text{ eV}^2$, implying that $K > 0.2 \text{ eV \AA}^{-2}$. However, as we have already mentioned, other choices for fixed ω_0 are possible, e.g., multiplying the rhs of (33) by a numerical constant might lead to a compatible condition $R > 1$ even for values of K as in [10]. Nevertheless, we believe that the particular *functional* relationship among the model parameters obtained in (42) distinguishes the corresponding analysis for the classical and quantum versions of the model. It would be desirable if such a relationship could be checked by experiments.

Note added. After the present work was completed, we became aware of another paper treating the Peyrard-Bishop model where the Morse potential was replaced by $V(u) = \frac{1}{2}Bu^2 - C\gamma u^3$ [F. Pitici and S. Svirshchevski, Phys. Rev. A **44**, 8348 (1991)]. Using a mean-field approach, the authors also looked for a translational invariant state of the system; however, they found a strong dependence of T_c on the number of particles N .

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[1] See, for example, Y. Gao and E. W. Prohovsky, J. Chem. Phys. **80**, 2242 (1984); Y. Gao, K. V. Devi-Prasad, and E. W. Prohovsky, *ibid.* **80**, 6291 (1984); Y. Kim, K. V. Devi-Prasad, and E. W. Prohovsky, Phys. Rev. B **32**, 5185

(1985).

[2] M. Peyrard and A. R. Bishop, Phys. Rev. Lett. **62**, 2755 (1989).

[3] *Handbook of Biochemistry—Molecular Biology*, 2nd ed.,

- edited by H. Sober (Chemical Rubber, Cleveland, 1970).
- [4] R. P. Feynman, *Statistical Mechanics—A Set of Lectures* (Addison Wesley, Reading, MA, 1972).
- [5] (a) K. G. Wilson, *Phys. Rev.* **179**, 1499 (1969); (b) M. A. Shifman, A. I. Vainshtein, and V. I. Zakharov, *Nucl. Phys.* **147**, 385 (1979).
- [6] S. Doniach and E. H. Sondheimer, *Green's Functions for Solid State Physicists*, revised ed. (Benjamin/Cummings, Reading, MA, 1978).
- [7] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, revised English ed. (Dover, New York, 1975).
- [8] P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
- [9] A. Mazur and B. Harrow, *Textbook of Biochemistry*, 10th ed (Saunders, Philadelphia, 1971).
- [10] T. Dauxois, M. Peyrard, and A. R. Bishop, *Phys. Rev. E* **47**, 684 (1993).