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How adsorption influences DNA denaturation

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The thermally induced denaturation of DNA in the presence of an attractive solid surface is studied. The two strands of DNA are modeled via two coupled flexible chains without volume interactions. If the two strands are adsorbed on the surface, the denaturation phase transition disappears. Instead, there is a smooth crossover to a weakly naturated state. Our second conclusion is that even when the interstrand attraction alone is too weak for creating a naturated state at the given temperature and also when the surface-strand attraction alone is too weak for creating an adsorbed state, the combined effect of the two attractions can lead to a naturated and adsorbed state.

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I. INTRODUCTION

The structure of DNA is the key for understanding its biological functioning, explaining why the physical features of DNA have attracted attention over the last decades [1–7]. A known component of this structure is the Watson-Crick double strandedness: DNA is composed of two single-strand molecules lined up by relatively weak hydrogen bonds. The double strand exists for physiological temperatures and is responsible for the stability of the genetic information stored in DNA. For higher temperatures the double strand separates into two strands (denaturation). Many processes relevant for the functioning of DNA—such as transcription and replication of the genetic information and packing of DNA into chromosomes—proceed via at least partial separation (denaturation) of the two strands due to breaking of hydrogen bonds [1,2]. In addition, denaturation is important for a number of technological processes, such as DNA sequence determination and DNA mechanical nanodevices [2].

DNA denaturation is driven by changing the temperature or the solvent structure—e.g., the pH factor [1,2]. There are several generations of statistical physics models aiming to describe the physics of denaturation. Early models, based on the one-dimensional Ising model, focus on the statistics of hydrogen bonds, modeling them as two-state variables (open or closed) [4]. More recent models describe a richer physics, in that they try to explore the space configurations of DNA [5–9].

Most of the physics literature devoted to DNA denaturation studies this process in isolation from other relevant processes involved in DNA functioning [3–10]. However, denaturation is frequently only a component of a larger process, such as replication or compactification into a nucleosome, the basic structural unit underlying the chromosome.

Here we want to study how another important aspect of DNA physics—adsorption of the double-strand DNA on a surface—influences its denaturation. Surface adsorption of DNA is widely employed in biotechnologies for immobilization and patterning (drug or gene delivery) of DNA [10,11]. There are in fact several pertinent situations, where both adsorption and denaturation of DNA are simultaneously at play.

(i) For DNA at normal conditions (pH$=7$ and NaCl concentration of 0.15 M) thermal denaturation occurs between temperatures 67 and 110 °C (which are the temperatures for A-T and C-G unbinding, respectively) [1,3,4]. The denaturation temperature can be decreased by increasing the pH factor—i.e., by decreasing the concentration of free protons in the solvent, since the negatively charged phosphate groups on each strand are not screened anymore by protons and strongly repel each other. For the same reason, for DNA adsorption on a positively charged surface, the increase of pH will increase the electrostatic attraction to the surface. Thus, at certain values of the pH factor and the surface charge, denaturation and adsorption may take place simultaneously.

(ii) Surface adsorption can be realized by the hydrogen bonding of negatively charged phosphate residues to a negative surface (e.g., silica surface) [10,12]. The effect is possible only when the electrostatic repulsion is sufficiently screened by the solvent cations. Thus the same factors (temperature, pH, solvent concentration) that decrease the interstrand attraction will weaken the DNA-surface binding [10].

(iii) The binding to hydrophobic surfaces (e.g., aldehyde-derivate glass or microporous membrane) goes via partial denaturation which exposes the hydrophobic core of the double helix and leads to the DNA-surface attraction [10]. Both naturation and adsorption are simultaneously weakened by increasing the pH [10,13].

(iv) Human DNA has a total length of 2 m, bearing a total charge of 10^8 electron charge units. This long object is contained in the cell nucleus with diameter 10 μm, which is comparable with the persistence length of DNA. Recall that the persistence length of a polymer is a characteristic length over which the polymer folds freely due to thermal fluctuations. For double-strand DNA at normal conditions, the persistence length is relatively large and amounts to 50 nm or 100 base pairs, while the persistence length of the single-stranded DNA is much smaller, about 1–2 nm (i.e., 2–4 base pairs) [14]. This seems to create a paradoxical situation: not only the large, strongly charged DNA has to be packed in a very small compartment, but the DNA has to be replicated, repaired, and transcribed. The problem is solved by a hierarchical structure: the DNA double helix is wrapped around positively charged histone (achieving partial charge neutralization), histones condense into a nucleosome complex, which in its turn is contained in chromatin, etc. It was recently discovered that packing of DNA into nucleosomes with a characteristic size much smaller than the persistence length of the DNA chain proceeds via transient denaturation of the double strand [15]. Denaturation reduces the persistence length and thereby facilitates the packing process.

For all these processes we need to describe the DNA as a double-strand polymer interacting with an attracting surface. This will be the goal of the present paper.

Needless to say, there is an obvious situation where the double-stranded structure is not relevant for the adsorption. If the two strands are too tightly connected, their separate motion is not resolved. This case is well known in the literature and—due to a large persistence length of a double-strand DNA—can be described via an effectively single semiflexible chain interacting with the surface [16]. These studies complement the classic theory of flexible chain adsorption, extensively treated in the literature [3,17,18]. The electrostatic effects of DNA adsorption, modeled via a single Gaussian chain, are studied in [19]. Another recent activity couples the Ising-Zimm-Bragg model for the helix-coil transition with the known theory of flexible chain adsorption on solid surfaces [20]. While interesting for their own sake, the results of Ref. [20] do not apply to DNA adsorption and denaturation, since the main assumption of Ref. [20]—that the helical pieces of the polymer interact with the surface much more strongly than the coiled ones—does not hold for DNA.

This paper is organized as follows. In Sec. II we define the model we shall work with. It describes two flexible chains interacting with each other and with an attracting solid surface. Section II also recalls the known correspondence between the equilibrium physics of flexible polymers and quantum mechanics. In its final part this section discusses limitations of the studied model in including volume interactions. Section III recalls the quantum-mechanical variational principle which will be the basic tool of our analysis. Section IV shows that if both polymers are adsorbed on the surface, they do not denaturate via a phase transition. Section V discusses collective scenarios of binding, while Sec. VI studies conditions under which the naturated and/or adsorbed state is certainly absent. The next section presents the phase diagram of the model. The last section summarizes our results. Some technical issues are discussed in appendixes. The reader interested in the qualitative message of this work may study Sec. II for learning the relevant notation and then jump to Sec. VII, which discusses general features of the phase diagram. A short account of the present work has appeared already in Ref. [21].

II. MODEL

When the motion of single strands is resolved—i.e., when the interstrand hydrogen bonds are relatively weak, as happens next to denaturation or unzipping transitions—DNA becomes a complex system with different, mutually balancing features at play. A realistic model of DNA should take into account the stacking energy between two base pairs and its dependence on the state (open or closed) of these pairs: helical structure of the double strand, intrastrand and interstrand volume interactions (e.g., self-avoidance), the pairing energy difference between A-T and C-G pairs (respectively, $3k_{\mathrm{B}}T$ and $5k_{\mathrm{B}}T$ under normal conditions), etc. Such fully realistic models do not seem to exist; there are, however, various models with different degrees of sophistication which are intended to capture at least some features of the double-stranded structure [3,5–10,16,17].

The model we shall work with disregards almost all the above complex aspects and focuses on the most basic features of the problem. It consists of two homogeneous flexible chains interacting with each other and coupled to the surface described as an infinite rigid attractive wall.

Consider $2N$ coupled classical particles (monomers) with radius vectors $\vec{r}_{1|k}$ and $\vec{r}_{2|k}$ $(k=1,\ldots,N)$ and potential energy

$$\Pi(\vec{r}_{\alpha|k}) = \sum_{k=1}^{N}\left\{\mathcal{U}(\vec{r}_k) + \sum_{\alpha=1}^{2}\left[\frac{K}{2}(\vec{r}_{\alpha|k}-\vec{r}_{\alpha|k-1})^2 + \mathcal{V}(\vec{r}_{\alpha|k})\right]\right\}, \tag{1}$$

where $\vec{r}_k \equiv \vec{r}_{1|k}-\vec{r}_{2|k}$, so that $|\vec{r}_{1|k}-\vec{r}_{2|k}|$ is the distance between two monomers, $\mathcal{U}$ is the interstrand potential, and $\mathcal{V}$ is the surface-monomer potential. The harmonic interaction with stiffness K (Gaussian chain) between successive monomers in each strand is responsible for the linear structure of the polymers.

The system is embedded in an equilibrium thermal bath at temperature $T=1/\beta$ $(k_{\mathrm{B}}=1)$. The quadratic kinetic energy of monomers is irrelevant, since it factorizes from the partition function and does not influence the equilibrium probability distribution:

$$P(\vec{r}_{\alpha|k}) = \frac{e^{-\beta\Pi(\vec{r}_{\alpha|k})}}{\mathcal{Z}}, \tag{2}$$

$$\mathcal{Z} = \int\left[\prod_{\alpha=1,2}\prod_{k=1}^{N} d\vec{r}_{\alpha|k}\right] e^{-\beta\Pi(\vec{r}_{\alpha|k})}. \tag{3}$$

This model without an adsorbing surface—i.e., $\mathcal{V}\equiv 0$—was mentioned in [17] and studied in [5] in the context of DNA denaturation. When the interstrand interaction $\mathcal{U}(r)$ is absent, we get two independent flexible chains interacting with the solid surface, a well-known model for adsorption-desorption phenomena [3]. Recall that our purpose is in studying these two processes—i.e., surface-polymer interaction and interstrand attraction—together. When taken separately, these processes are well studied and well understood.

Note that for the considered Gaussian chain model the stiffness parameter K relates to the characteristic persistence length l_p as [3]

$$K = \frac{T}{l_p^2}. \tag{4}$$

A. Specification of the surface-monomer potential

We assume that the surface can be represented as an infinite, solid plane at $z=0$ (the role of the solid surface can be played by any body of a smooth shape and size much larger than the polymer length). Thus for the probability distribution (2) one has (for $\alpha=1,2$ and $k=1,\ldots,N$)

$$P(\vec{r}_{\alpha|k}) = P(x_{\alpha|k}, y_{\alpha|k}, z_{\alpha|k}) = 0, \quad \text{for } z_{\alpha|k} \leqslant 0. \tag{5}$$

This boundary condition should be imposed as a constraint in (2).

The remaining part of the surface-strand interaction is described by a negative (attractive) potential $\mathcal{V}$ that depends only on the third coordinate: $\mathcal{V}(\vec{r}_{\alpha|k})=\mathcal{V}(z_{\alpha|k})$. The potential $\mathcal{V}(z)$ will be assumed to be short ranged: it is negative for $z\to 0$ and tends to zero sufficiently quickly for $z\to\infty$.

Let us continue the specification of the potential $\mathcal{V}(z)$, taking as an example the electrostatic attraction between one negatively charged DNA strand and a positively charged surface; see, e.g., [18]. We denote by σ the surface charge density, q stands for the monomer charge (for DNA the effective monomer charge is roughly $q\simeq 1e$, where e is the electron charge), and ϵ is the dielectric constant of the medium into which the polymer is embedded ($\epsilon\approx 80$ for water at room temperature). Now the interaction energy between the surface area $dxdy$ and one monomer reads

$$\frac{q\sigma}{\epsilon r} e^{-k_{\mathrm{D}} r} dx dy, \tag{6}$$

where $r=\sqrt{x^2+y^2+z^2}$ is the distance between the surface area $dxdy$ and the monomer, while k_{D} is the inverse Debye screening length. This interaction leads to an attraction for opposite charges: $q\sigma<0$. The full expression of the inverse Debye screening length is well known:

$$k_{\mathrm{D}} = \sqrt{2\pi l_{\mathrm{B}} \sum_a n_a Z_a^2}, \quad l_{\mathrm{B}} \equiv \frac{e^2}{\epsilon T}, \tag{7}$$

where l_{B} is the Bjerrum length and n_a and Z_a are, respectively, the concentration and valency of ions of the sort a present in the solvent (so that the ion charge is $Z_a e$). The summation in (7) is taken over all sorts of ions present.[1] Under normal conditions the Bjerrum length is $\simeq 1$ nm. At this length the electrostatic interaction energy becomes comparable with the thermal energy T. The Debye length $1/k_{\mathrm{D}}$ varies between ~ 0.5 and ~ 1.5 nm under physiological conditions. For pure water it is much longer: $1/k_{\mathrm{D}}\sim 1$ μm.

Integrating (6) over x and y from $-\infty$ to $+\infty$, we get for the surface-monomer interaction [18]

$$\mathcal{V}(z) = \frac{2\pi q\sigma}{\epsilon k_{\mathrm{D}}} e^{-k_{\mathrm{D}} z}. \tag{8}$$

Thus the strength of the potential is $\frac{2\pi q\sigma}{\epsilon k_{\mathrm{D}}}$, while the inverse characteristic length is (expectedly) $1/k_{\mathrm{D}}$. The potential $\mathcal{V}(z)$ is short ranged for all other relevant mechanisms of adsorption (hydrogen binding, hydrophobic interactions, cation exchange). This means, in particular, that $\int_0^\infty dz \mathcal{V}(z)$ is finite for all these mechanisms [22].

Returning to (8), we note that for a single flexible polymer interacting with the surface the adsorption problem was solved in Ref. [18] within the Schrödinger equation approach, to be discussed below in detail; see, in particular, Eq. (23). The adsorption-desorption phase-transition temperature found in [18] reads

$$T_c = \frac{8.33\pi|\sigma q|}{k_{\mathrm{D}}^3 l_p^2 \epsilon}, \tag{9}$$

where l_p is the persistence length from (4).

Let us estimate the Debye length as $k_{\mathrm{D}}^{-1}\sim 1$ nm and the single-polymer persistence length as $l_p\sim 1$ nm, and assume that the surface contains Z elementary (electron) charges per 1 nm × 1 nm. Normally $Z\sim 1$, though strongly charged surfaces achieve $Z=10-20$. Taking the effective monomer charge-1 elementary charge (which is a typical value for a single-strand DNA) and recovering the Boltzmann constant, we see that (9) predicts T_c of order of room temperature (300 K).

When looking at the concrete parameters in (9), we should also recall that Eqs. (6)–(8) account for the surface-monomer electrostatic interaction, while the monomer-monomer electrostatic interaction within the single polymer is neglected. This is possible when the surface charge σl_p^2 at the area $l_p\times l_p$ (where l_p is the persistence length of the single strand) is larger than the monomer charge:

$$\sigma l_p^2 \gg |q|. \tag{10}$$

This condition will be satisfied for strongly charged surfaces $Z\approx 10$.

B. Specification of the monomer-monomer interaction between the two strands

The interstrand potential $\mathcal{U}(|\vec{r}_{1|k}-\vec{r}_{2|k}|)$ collects the effects of hydrogen bonding, (partial), stacking, and possible electrostatic repulsion. We again assume that it is purely attractive, short ranged, and goes to zero sufficiently fast whenever the interparticle distance $|\vec{r}_{1|k}-\vec{r}_{2|k}|$ goes to infinity. In particular, the short-range features imply that $\int_0^\infty dr\, r^2 U(r)$ is finite.

Several concrete examples of the interstrand potential $\mathcal{U}$ were studied and favorably compared with denaturation experiments in [5–7]. For example, Ref. [6] studies the Morse potential

$$\mathcal{U}(r) = \nu e^{-ar}(e^{-ar}-2), \tag{11}$$

where ν is the potential strength and $\frac{1}{a}$ is its characteristic range. Within the Schrödinger equation approach [see (23) below] Eq. (11) predicts a second-order denaturation transition at the critical temperature

$$T_c = \frac{16\nu}{a^2 l_p^2}. \tag{12}$$

Note that the appearance of the factor $a^2 l_p^2$ in (12) is similar to the that of the factor $k_{\mathrm{D}}^2 l_p^2$ in (9). Here are the standard

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[1] The quantity $\frac{1}{2}\Sigma_a n_a Z_a^2$ is called ionic strength.

estimates for the parameters in (12): $\nu \simeq 0.01$ eV, $l_p \simeq 1$ nm, and $al_p \simeq 2$ [7]. These produce from (12) $T_c \sim 400$ K, which by an order of magnitude coincides with experimental values [7].

C. Effective Schrödinger equation

It is known (see, e.g., [3,7]) that in the thermodynamical limit $N \gg 1$ the free energy of flexible polymers in an external potential is determined from an effective Schrödinger equation; see Appendix A for more details. A sufficient condition for the validity of the Schrödinger equation approach is that the characteristic length D over which the polymer density changes is much larger than the persistence length l_p:

$$D \gg l_p. \tag{13}$$

This condition is always satisfied in the vicinity of a second-order phase-transition, where D is naturally large for a fixed l_p. If condition (13) is satisfied for a short-range potential—see (8) and (12) for relevant examples—this potential is necessarily small for those distances $\sim D$, where the flexible polymer is predominantly located [3].

For the considered two-strand situation, the Schrödinger equation reads

$$H\Psi = E\Psi, \tag{14}$$

$$H \equiv \sum_{\alpha=1}^{2} \left(-\frac{1}{2}\partial_{\vec{r}_\alpha}^2 + V(z_\alpha) \right) + U(r), \tag{15}$$

where [using also (4)]

$$V(z) \equiv K\beta^2 \mathcal{V}(z) = \frac{\beta}{l_p^2}\mathcal{V}(z), \quad U(r) \equiv K\beta^2 \mathcal{U}(r) = \frac{\beta}{l_p^2}\mathcal{U}(r). \tag{16}$$

If there is a gap between the lowest two eigenvalues of H, the ground-state wave function Ψ determines the monomer statistics as

$$n(\vec{r}_1,\vec{r}_2) = \Psi^2(\vec{r}_1,\vec{r}_2), \tag{17}$$

where $n(\vec{r}_1,\vec{r}_2)$ is the probability distribution for two neighboring monomers on the strands for the considered translationally invariant system.

Recalling the known correspondence between the flexible polymer physics and (stationary) quantum mechanics [3], we can think of $\vec{r}_{1,2}=(x_{1,2},y_{1,2},z_{1,2})$ as the position vectors of two quantum particles representing the strands, while $\vec{r}=\vec{r}_1-\vec{r}_2$ is their mutual position.

The eigenvalue E is the energy of the quantum pair. It is related to the free energy fN of the system as

$$E = \beta^2 lf + 3\beta l \ln \frac{2\pi}{\beta l}. \tag{18}$$

Since the surface is described by an infinite potential wall, we have the following boundary condition for the wave function:[2]

$$\Psi(\vec{r}_1,\vec{r}_2) = 0, \quad \text{if } z_1 \leq 0 \text{ or } z_2 \leq 0. \tag{19}$$

Both $V(z)$ and $U(r)$ are attractive, $V \leq 0, U \leq 0$, and short ranged; that is $\int_0^\infty dz\, V(z)$ and $\int_0^\infty dr\, r^2 U(r)$ are finite. When $U=0$, the Hamiltonian H reduces to two uncoupled strands (or two uncoupled quantum particles), each one in the potential $V(z)$. The corresponding Schrödinger equation for the z coordinate of one strand reads from (15)

$$\left(-\frac{1}{2}\partial_z^2 + V(z) \right)\psi(z) = E\psi(z), \quad \psi(z=0) = 0. \tag{20}$$

It is well known that if $V(z)$ is shallow enough, no bound (negative energy) state exists, while the second-order binding transitions correspond to adsorption of a single flexible polymer [3]. The physical order parameter for this transition is the inverse square average distance from the surface, $1/\langle z^2 \rangle$, which is finite (zero) in the adsorbed (desorbed) state. It is useful to denote by μ the dimensionless coupling constant of $V=\mu\tilde{V}$ such that (for $U=0$) the adsorption threshold is

$$\mu_{c,0} = 1. \tag{21}$$

Note that the adsorption of single-strand DNA is a part of the renaturation via hybridization [2], a known method of genetic systematics.

For the example (8) the concrete expression for μ reads from (9)

$$\mu = \frac{8.33\pi|\sigma q|}{Tk_{\mathrm{D}}^3 l_p^2 \epsilon}. \tag{22}$$

Analogously, switching off both $V(z)$ and the wall, we shall get a three-dimensional central-symmetric motion in the potential $U(r)$, which again is not bound if U is shallow. This second-order unbinding transition with the order parameter $1/\langle r^2 \rangle$, where r is the interstrand distance, corresponds to thermal denaturation (strand separation) of the double-strand polymer [1,2,5,7].

The Schrödinger equation for the radial motion in the absence of the surface reads from (15) [7]

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[2] In fact, one should be more careful when defining the boundary condition (19). For the two-particle case, it appears to be necessary to fix not only the continuity of Ψ and its value at the wall, as Eq. (19) does, but also the behavior next to the wall: one has to require that when z_1 and z_2 go to zero simultaneously, $\Psi \propto z_1 z_2$. Otherwise, there will be (continuous) wave functions which provide a bound state for two particles with an arbitrarily weak $V<0$ and arbitrary weak interparticle interaction $U<0$, though the single particle needs a critical strength of V to get into a bound state. This obviously pathological situation is prevented by the additional boundary condition $\Psi \propto z_1 z_2$. For the wave functions we shall consider below, this additional boundary condition will be satisfied automatically.

$$\left(-\frac{1}{4}\partial_r^2+U(r)\right)\chi(r)=E\chi(r),\quad \chi(r=0)=0, \tag{23}$$

where $\chi(r)$ is related to the original wave function as

$$\psi(r)=\frac{\chi(r)}{r}. \tag{24}$$

Note that (23) is again a one-dimensional Schrödinger equation, but as compared to Eq. (20), Eq. (23) contains an additional factor of $\frac{1}{2}$ next to the kinetic-energy term ∂_r^2. This factor arises due to effective mass; see [22] for more details.

Let us write likewise $U=\lambda\tilde{U}$, where λ is the dimensionless naturation strength. We take the naturation threshold in the bulk to be

$$\lambda_{c,0}=1. \tag{25}$$

For the example (11), λ reads from (12)

$$\lambda=\frac{16\nu}{a^2 l_p^2 T}. \tag{26}$$

When the wall is included—i.e., when condition (19) is imposed—the strands lose in the adsorbed phase part of their entropy. This is known to lead to a fluctuation induced effective repulsion [23].

Let us now recall that the physics of weakly bound quantum particles does not depend on details of the binding potential [22]. Thus for a qualitative understanding of the situation one may employ the δ-shell potential, which is easily and exactly solvable and has very transparent physical features; see Appendix B.

D. Relevant coordinates

Let us now return to the basic equation (20). It is convenient to recast this equation in new coordinates:

$$v_1=\frac{1}{2}(x_1+x_2),\quad v_2=\frac{1}{2}(y_1+y_2), \tag{27}$$

$$x_1-x_2=\rho\cos\varphi,\quad y_1-y_2=\rho\sin\varphi, \tag{28}$$

where

$$0\leqslant\rho,\quad 0\leqslant\phi\leqslant 2\pi, \tag{29}$$

and to rewrite the Schrödinger equations (14) and (15) as

$$-\frac{1}{2}\left\{\frac{2}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial}{\partial\varphi}+\frac{1}{2}\frac{\partial^2}{\partial v_1^2}+\frac{1}{2}\frac{\partial^2}{\partial v_2^2}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right\}\Psi$$
$$+\{V(z_1)+V(z_2)+U(|\vec{r}_1-\vec{r}_2|)\}\Psi=E\Psi. \tag{30}$$

It is seen from (30) that the variables separate, since $\Psi(\vec{r}_1,\vec{r}_2)$ can be written as

$$\Psi(\vec{r}_1,\vec{r}_2)=\psi(\rho,z_1,z_2)\psi_1(v_1)\psi_2(v_2)\psi_3(\varphi), \tag{31}$$

and the lowest-energy levels are to be found via the equation

$$-\frac{1}{2}\left\{\frac{2}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}+\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right\}\Psi+\{V(z_1)+V(z_2)$$
$$+U(\sqrt{\rho^2+(z_1-z_2)^2})\}\Psi=E\Psi. \tag{32}$$

Thus, due to the translational invariance along the surface and the invariance under rotations around the z axis, we are left with three independent coordinates: the projection ρ of the interparticle distance on the surface and the distances z_1 and z_2 between the particles and the surface.

Note that within the quantum-mechanical setting the problem described by (32) corresponds to a three-body problem in $d=3$, where the role of the third body (with infinite mass) is played by the surface.

E. Common action of the surface-strand and interstrand potentials

In this and the subsequent subsection, we shall discuss two possible limitations of the present model.

Above we combined together the surface-strand interaction potential $\mathcal{V}$, which was derived separately from studying interaction of the surface with one flexible strand, and interstrand potential $\mathcal{U}$ deduced from studying two flexible strands without the surface. While this type of combining is widely applied in all areas of statistical physics, its applicability needs a careful discussion in each concrete case. For instance, it is possible that the presence of an adsorbing surface will directly influence the interstrand potential. Let us discuss one (perhaps the major) example of that type pertinent for the model studied.

It is well known that the two strands of DNA are negatively charged [1]. For double-stranded DNA under normal conditions, the interstrand repulsion is screened by positive counter-ions, so that the hydrogen bonding can overcome the electrostatic repulsion and create an effective attraction, which is then the main reason for interstrand binding [1]. Once DNA denaturates and separates into two strands, the counter-ions are released into the ambient medium and are clouded around each strand. However, for temperatures not very far from the denaturation temperature, the counter-ions continue to screen the electrostatic repulsion, so that once the temperature lowers below the denaturation transition temperature, the two strands reversibly assemble back into the double strand [1]. We stress that the fact that (partially released) counter-ions still provide a sufficient screening follows from the existence of the observed reversible renaturation transition.

When DNA denaturates in the presence of a positively charged surface, the cloud of screening counter-ions around each strand will tend to rarefy. This will increase the screening length and make the overall interstrand interaction repulsive. However, this is possible only for strongly adsorbed strands, where the majority of counter-ions are within the direct influence of the surface charge. In the present work we focus on weakly bound strands, where the characteristic length of the adsorbed layer, D, is much larger than the persistence length l_p (approximately 1 nm in normal conditions), which is of the same order of magnitude as the Debye screening length $1/k_{\mathrm{D}}$; see (13). Thus the majority of counter-ions will not feel the adsorbing surface, and in this case we do not need to account directly for the influence of the surface on the interstrand potential. For strongly adsorbed DNA strands—i.e., for $D\sim 1/k_{\mathrm{D}}$—it can be necessary to couple directly the interstrand potential with the degree of adsorption.

F. Self-avoidance and of electrostatic volume interactions

In Hamiltonian (1) we accounted for the surface-strand and interstrand interactions, but neglected all the volume interactions such as self-avoidance and the (for charged polymers) electrostatic interaction between various monomers. It is important to note that the volume interactions coming from the intrachain contributions can be accounted for within the present model via renormalizing the persistence length l_p; see (1) and (4) for definitions. As shown in [24] for a single flexible polymer interacting with electrostatically adsorbing surface, the self-avoiding interactions and electrostatic volume interactions renormalize the persistence length. Provided that the Debye screening length $1/k_{\mathrm{D}}$ is not very large—a sufficient condition for this is $k_{\mathrm{D}} l_p \sqrt{N} \gg 1$, where N is the number of monomers [24]—both self-avoiding and electrostatic volume interactions lead to an effective persistence length $\tilde{l}_p$, which differs from the bare persistence length mainly by the factor $N^{1/10}$: $\tilde{l}_p \sim N^{1/10} l_p$ [24] (the remaining part of renormalization is numerical factors, which are not essential for the present qualitative discussion).[3] Once the persistence length is renormalized, one can still use the flexible polymer coupled to an adsorbing surface [24]. Thus the transition temperatures (9) and (12) are divided by a factor of $N^{1/5}$, where N is the number of monomers. Now, for the typical single-strand DNA length $N \sim 10^4$, this renormalization will not make any substantial change in the transition temperatures, though it is essential for longer polymers, $N \geqslant 10^5$. In particular, for such a long polymer the persistence length may increase to an extent that the condition (13) will be violated.

We will see below that for the qualitative conclusions of this paper, the precise form of the renormalized persistence length is not essential, provided that one can still employ the Schrödinger equation (20) for describing denaturation and desorption. The main reason for this is that the renormalization of the persistence length homogeneously renormalizes both dimensionless couplings λ and μ in (25) and (21), respectively.

The above discussion does not account for the interchain volume interactions and thus should not create an impression that the full volume interaction effect for two coupled chains can be described via a renormalized persistence length. It is clear that one needs a more specific study of volume interactions for the present model. Since such a study poses imminent analytical problems, it will be concluded at a later time.

III. VARIATIONAL PRINCIPLE AND THE EXISTENCE OF THE OVERALL BOUND STATES

Note that Eqs. (19) and (32) follow from a variational principle

$$\delta \mathcal{I}\{\psi\} = 0, \tag{33}$$

with

$$\mathcal{I}\{\psi\} = \int_0^\infty \int_0^\infty \int_0^\infty \rho d\rho dz_1 dz_2 \Bigg[\frac{1}{4}\Bigg\{ 2\left(\frac{\partial \psi}{\partial \rho}\right)^2 + \left(\frac{\partial \psi}{\partial z_1}\right)^2 + \left(\frac{\partial \psi}{\partial z_2}\right)^2 \Bigg\} + \frac{1}{2}\{V(z_1) + V(z_2) + U(\sqrt{\rho^2 + (z_1 - z_2)^2}) - E\}\psi^2 \Bigg] = 0, \tag{34}$$

where ψ is taken real, since we are interested in bounded (discrete-level) states. We already assumed that ψ is properly normalized:

$$\int_0^\infty \int_0^\infty \int_0^\infty \rho d\rho dz_1 dz_2 \psi^2(z_1, z_2, \rho) = 1. \tag{35}$$

If either $V(z)=0$ or $U=0$, the criterion for the existence of a bound state is well known, since it reduces to the existence of a negative energy in the spectrum or, equivalently, to the existence of a physically admissible (satisfying the proper boundary conditions) wave function with a negative average energy.

The situation is slightly more delicate when the two potentials V and U act together. Let us assume that either for $V(z) \to 0$ or for $U(|\vec{r}_1 - \vec{r}_2|) \to 0$ there are negative-energy states. Denote by

$$E\{U\} < 0, \quad E\{V(z_1) + V(z_2)\} = 2E\{V\} < 0, \tag{36}$$

respectively, the corresponding lowest (most negative) energies.

Then it suffices to have a normalized wave function ψ with

$$\mathcal{I}\{\psi\} < E\{U\} + 2E\{V\}, \tag{37}$$

for at least one overall bound—i.e., adsorbed and naturated—state to exist.

IV. ABSENCE OF A DENATURATION PHASE TRANSITION FOR ADSORBED STRANDS

Let us return to the variational principle (34) and assume that $V(z)$ is strong enough to create at least a single (lowest) bound state with energy $E\{V\} < 0$. Denote by $\phi(z)$ the corresponding lowest-energy normalized wave function:

$$-\frac{1}{2}\phi''(z) + V(z)\phi(z) = E\{V\}\phi(z). \tag{38}$$

For the overall problem we shall employ the following variational wave function:

$$\psi(\rho, z_1, z_2) = \phi(z_1)\phi(z_2)\xi(\rho), \tag{39}$$

where $\xi(\rho)$ is an unknown, tentatively normalized, viz.,

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[3] In more detail, Ref. [25] considers a continuous polymer model with length L and reports for the square of the effective persistence length $\tilde{l}_p^2 \sim L^{1/5} l_p^2$. For the present discrete model, we take naturally $L \propto N$.

$$\int_0^\infty d\rho\, \rho \xi^2(\rho) = 1, \tag{40}$$

wave function, to be determined from the optimization of (34). Note that in (39) the boundary conditions for the surface are satisfied via $\phi(z_1)\phi(z_2)$.

Substituting (39) into (34) and varying it over ξ, we get an effective Schrödinger equation for $\xi(\rho)$

$$-\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho}\right\}\xi + \{U_{\rm eff}(\rho) - \varepsilon\}\xi = 0, \tag{41}$$

where $U_{\rm eff}(\rho)$ is an effective potential:

$$U_{\rm eff}(\rho) = \int_0^\infty dz_1 \int_0^\infty dz_2 \phi^2(z_1)\phi^2(z_2) U(\sqrt{\rho^2 + (z_1 - z_2)^2}), \tag{42}$$

and where ε is the reduced energy

$$\varepsilon = E - 2E\{V\}. \tag{43}$$

Two main points about the effective potential (42) is that it is attractive (since so is U) and goes to zero for $\rho \to \infty$. The last feature follows from the analogous one of $U(r)$ and the fact that $\phi(z)$ are normalizable. A more explicit form for $U_{\rm eff}$ can be obtained by assuming that $U(r)$ is a δ-shell potential:

$$U(r) = -\frac{\lambda}{r_0}\delta(r - r_0), \tag{44}$$

with strength $\lambda > 0$ and attraction radius $r_0 > 0$. The transparent properties of this potential are recalled in Appendix B. The critical binding strength of this potential is

$$\lambda_{c,0} = 1, \tag{45}$$

as given by (B9). [When comparing Eq. (44) with Eq. (B2), note that the additional factor of 2 comes from the reduced mass.]

Using (44), we now obtain from (42) after changing variables

$$\begin{aligned} U_{\rm eff}(\rho) &= -\frac{\lambda}{r_0}\int_0^\infty dv \int_0^v du\, \phi^2\left(\frac{v+u}{2}\right)\phi^2\left(\frac{v-u}{2}\right) \\ &\quad \times \delta(\sqrt{\rho^2 + u^2} - r_0) \\ &= -\lambda\frac{\theta(r_0 - \rho)}{\sqrt{r_0^2 - \rho^2}}\int_{\sqrt{r_0^2-\rho^2}}^\infty dv\, \phi^2\left(\frac{v + \sqrt{r_0^2 - \rho^2}}{2}\right) \\ &\quad \times \phi^2\left(\frac{v - \sqrt{r_0^2 - \rho^2}}{2}\right) \\ &= -2\lambda\frac{\theta(r_0 - \rho)}{\sqrt{r_0^2 - \rho^2}}\int_0^\infty dv\, \phi^2(v + \sqrt{r_0^2 - \rho^2})\phi^2(v). \end{aligned} \tag{46}$$

It is now seen explicitly that $U_{\rm eff}(\rho)$ is zero for sufficiently large ρ.

Note that (41) has the form of the two-dimensional Schrödinger equation for an effective particle in the attractive potential $U_{\rm eff}(\rho)$. It is well known that any (however weak) attractive potential in two dimensions creates a bound state [22]. Thus there is a normalizable function $\xi(\rho)$ such that ε in (42) is negative. This means that

$$E < 2E\{V\}, \tag{47}$$

and, according to our discussion in Sec. III, there is an overall bound (naturated and adsorbed) state provided $V(z)$ creates a bound state. In our model a sufficiently attractive surface potential confines fluctuations of the two strands and prevents the denaturation phase transition (this, however, does not mean that the denaturation is absent as a physical process; see below).

The physical reason for the existence of an overall bound state for an arbitrary small potential is a peculiar two-dimensional effect: the weakly singular attractive $\propto 1/\rho^2$ potential [23].[4] Indeed changing in (41) the variables as

$$\tilde{\xi} = \frac{\xi}{\sqrt{\rho}}, \tag{48}$$

we get

$$-\frac{\partial^2\tilde{\xi}}{\partial^2\rho} + \left\{U_{\rm eff}(\rho) - \frac{1}{4\rho^2} - \varepsilon\right\}\tilde{\xi} = 0. \tag{49}$$

Equation (48) implies

$$\tilde{\xi}(0) = 0, \tag{50}$$

i.e., the existence of the infinite wall at $\rho=0$ for the effectively one-dimensional equation (49). It is, however, seen from (49) that there is also an attractive potential $1/(4\rho^2)$. It is known that if the strength of such a potential is larger than $1/4$ seen in (49), the (effective) quantum particle will fall to zero; i.e., the ground state will be minus infinity [22]. The value $1/4$ is just at the border of this phenomenon and, therefore, any attractive short-range potential acting in addition to $1/(4\rho^2)$ suffices to create a bound state [23].

To illustrate the behavior of $U_{\rm eff}$ for a weakly bound state of the potential $V(z)$, let us assume that $V(z)$ is also a δ-shell potential:

$$V(z) = -\frac{\mu}{2z_0}\delta(z - z_0). \tag{51}$$

Recall that we still have an infinite wall at $z=0$ and that for the δ-shell potential the bound state exists for

$$\mu > \mu_{c,0} = 1; \tag{52}$$

see Appendix B for details. If now μ is close to 1, the energy $E\{V\} \equiv -k^2/2$ is small. Working out (46) with the help of Eq. (B11), which essentially reduces to

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[4] The one-dimension case in this respect is not much different from the three-dimensional situation. The known statement on the existence of a bound state for any small one-dimensional potential is connected with a different mechanism—that is, with allowing all values of the one-dimensional coordinate (no infinite wall at the origin). The two-dimensional situation is indeed peculiar in this respect.

$$\phi(z) \propto \sqrt{2k}e^{-kz}, \tag{53}$$

we get

$$U_{\text{eff}}(\rho) = -2\lambda k \frac{\theta(r_0-\rho)}{\sqrt{r_0^2-\rho^2}}. \tag{54}$$

Since for small k the wave function $\psi(x)$ is almost delocalized, the effective potential $U_{\text{eff}}(\rho)$ is proportional to k and goes to zero for $k\to 0$—that is, for $\nu\to 1$. In other words, the trial function (39) does not predict any (overall) binding for

$$\mu \leqslant 1. \tag{55}$$

Note however that although for $\mu > 1$ any interstrand attraction is able to prevent the denaturation phase transition, the energy ε in (49) is exponentially small for small U_{eff}—i.e., small λ or small k. Recall that this energy is estimated as [22]

$$\varepsilon \simeq \frac{2}{r_0^2}\exp\left[2\int_0^\infty d\rho\,\rho U_{\text{eff}}(\rho)\right] = \frac{2}{r_0^2}e^{-1/(\lambda k r_0)}. \tag{56}$$

Thus for a small λ or k we get a very large separation between the strands. In this sense the (incomplete) denaturation phenomenon without the phase transition is present in our model.

In summary, the main physical message of this section is that if the two strands are localized near the surface, the overall DNA molecule does not melt via a phase transition with increasing the temperature: there is only a smooth crossover from a tightly bound to a (very) weakly bound state. The cause of this effect is that the surface confines fluctuations of each strand. Mathematically this is expressed by an additional attractive potential $-\frac{1}{4\rho^2}$ in (49).

This result was obtained without taking into account various realistic features of DNA. It is possible that the denaturation transition in the adsorbed phase will recover upon taking into account some of those neglected features—e.g., volume interactions between the two strands and within each strand (see [9] for a prediction of such a transition in a different model of DNA that partially accounts for volume interactions).

We nevertheless expect that the obtained result will apply, at least qualitatively, to denaturation-renaturation experiments and will be displayed by facilitation of the naturation in the adsorbed phase. We are not aware of any specific experiment done to check the renaturation-facilitating effect of an attractive surface. There are, however, somewhat related experiments showing that the renaturation rate can significantly increase in the condensed (globular) phase of single-strand DNA [25]. This condensed phase is created by volume (monomer-monomer) interactions. The effect was obtained under a rather diverse set of conditions, but to our knowledge it did not get any unifying explanation. The analogy with our finding is that in the condensed phase fluctuations of the single-strand DNA are also greatly reduced as compared to a coil(-free) state.

V. COLLECTIVE BINDING

With the aim to understand the situation when $V(z)$ alone does not provide any binding, we take for the variational function

$$\psi(z_1,z_2,\rho) = \phi(z_1,z_2)\xi(\rho). \tag{57}$$

As compared to (39), we do not require that z_1 and z_2 be factorized, and we are going to optimize over $\phi(z_1,z_2)$. In contrast, $\xi(\rho)$ is a fixed, normalized [see (40)] known function.

Substituting (57) into (34) and varying over $\phi(z_1,z_2)$, we get

$$-\frac{1}{2}\left\{\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right\}\phi + \{V(z_1)+V(z_2)+V_{\text{eff}}(|z_1-z_2|)-E_1\}\phi = 0, \tag{58}$$

where

$$V_{\text{eff}}(z) \equiv \int_0^\infty d\rho\rho\xi^2(\rho)U(\sqrt{\rho^2+z^2}). \tag{59}$$

Recall that by the very meaning of the variational approach E_1 provides—for any λ and any normalized function $\xi(\rho)$—an upper bound for the real ground-state energy. Equation (58) describes two one-dimensional particles with interparticle interaction $V_{\text{eff}}(|z_1-z_2|)$ and coupled to an external field $V(z)$.

For the interparticle interaction given as in (44), this effective potential $V_{\text{eff}}(z)$ reads

$$V_{\text{eff}}(z) = -\lambda\,\theta(r_0-z)\xi^2(\sqrt{r_0^2-z^2}). \tag{60}$$

We are now going to show that Eq. (58) predicts binding—that is, it predicts $E_1<0$ and a localized normalizable wave function $\phi(z_1,z_2)$—at the critical point $\mu=1$ of the potential $V(z)$. To this end let us calculate the perturbative correction ΔE introduced by the effective potential V_{eff}. At first glance the application of perturbation theory is problematic, because we search for a nearly degenerate energy level. However, due to strong delocalization of the corresponding wave function, the matrix elements of the perturbing potential V_{eff} appear to be small as well, and applying perturbation theory is legitimate. This will be also underlined below by a perfectly finite behavior of the second-order perturbation theory result.

Recall that in the first two orders of the perturbation theory we have [22]

$$\Delta E \equiv E_1 - 2E\{V(z)\} = \langle 0|V_{\text{eff}}|0\rangle - \int_0^\infty dK\frac{|\langle 0|V_{\text{eff}}|nK\rangle|^2}{\varepsilon_K - 2E\{V\}}, \tag{61}$$

$$2E\{V\} = -k^2, \tag{62}$$

where $\langle z_1,z_2|0\rangle = \phi(z_1)\phi(z_2)$ is the lowest-energy state of the unperturbed system and where the integration over K involves all excited wave functions of the unperturbed two-particle system with wave vector K and energy ε_K (all these wave functions are in the continuous spectrum). Note that there are three orthogonal families of these states:

$$\phi(z_1)\tilde{\phi}(nz_2,n), \quad \varepsilon_n = \frac{n^2}{2} - \frac{k^2}{2}, \tag{63}$$

$$\phi(z_2)\tilde{\phi}(nz_1,n), \quad \varepsilon_n = \frac{n^2}{2} - \frac{k^2}{2}, \tag{64}$$

$$\tilde{\phi}(nz_1,n_1)\tilde{\phi}(nz_2,n_2), \quad \varepsilon_{n_1 n_2} = \frac{n_1^2}{2} + \frac{n_2^2}{2}, \tag{65}$$

where $\tilde{\phi}(nz,n)$ are the corresponding single-particle excited (continuous spectrum) wave function with wave number n. These wave functions are normalized over the wave-number scale; see Eq. (B14) in Appendix B. This type of normalization is important for integration over the wave number K in (61).

The first-order contribution to ΔE appears to be zero for $k \to 0^+$ (i.e., for $\mu \to 1^+$). Indeed, we can use (53) for

$$\phi(z_1,z_2) = \phi(z_1)\phi(z_2) = 2ke^{-k(z_1+z_2)}, \tag{66}$$

to conclude

$$\begin{aligned}\langle 0|H|0\rangle &= \int_0^\infty \int_0^\infty dz_1 dz_2 V_{\text{eff}}(|z_1-z_2|)\phi^2(z_1)\phi^2(z_2)\\ &= \int_0^\infty dv \int_0^v du V_{\text{eff}}(u)\phi^2\left(\frac{v+u}{2}\right)\phi^2\left(\frac{v-u}{2}\right)\\ &= 2k\int_0^\infty dv\, e^{-2kv}\int_0^v du V_{\text{eff}}(u) = O(k).\end{aligned} \tag{67}$$

Using (63)–(66), we shall calculate various matrix elements entering into (61):

$$\begin{aligned}\langle 0|H|n\rangle &= \int_0^\infty \int_0^\infty dz_1 dz_2 \phi(z_1)\phi(z_2) V_{\text{eff}}\\ &\quad\times(|z_1-z_2|)\phi(z_1)\tilde{\phi}(nz_2,n)\\ &= \sqrt{2k}2k\int_0^\infty dv\int_0^v du e^{-k(3v+u)/2}V_{\text{eff}}(u)\tilde{\phi}\left(\frac{n(u+v)}{2},n\right),\end{aligned} \tag{68}$$

$$\begin{aligned}\langle 0|H|n_1,n_2\rangle &= \int_0^\infty \int_0^\infty dz_1 dz_2 \phi(z_1)\phi(z_2) V_{\text{eff}}\\ &\quad\times(|z_1-z_2|)\tilde{\phi}(nz_1,n)\tilde{\phi}(nz_2,n)\\ &= 2k\int_0^\infty dv\int_0^v du e^{-kv/2}V_{\text{eff}}(u)\tilde{\phi}\left(\frac{n_1(u+v)}{2},n_1\right)\\ &\quad\times\tilde{\phi}\left(\frac{n_2(v-u)}{2},n_2\right).\end{aligned} \tag{69}$$

This results in the following formula for ΔE:

$$\Delta E = -2\int_0^\infty dn \frac{|\langle 0|H|n\rangle|^2}{\frac{n^2}{2}+\frac{k^2}{2}} - \int_0^\infty dn_1 dn_2 \frac{|\langle 0|H|n_1,n_2\rangle|^2}{\frac{n_1^2}{2}+\frac{n_2^2}{2}+\frac{k^2}{2}}. \tag{70}$$

Working this out and going to the limit $k \to 0^+$ (i.e., $\mu \to 1^+$), we obtain

$$\begin{aligned}\Delta E = -8\left[\int_0^\infty du V_{\text{eff}}(u)\right]^2 &\times\left\{4\int_0^\infty \frac{dn}{1+n^2}\left[\int_0^\infty dv e^{-3v/2}\tilde{\phi}\left(\frac{nv}{2},0\right)\right]^2\right.\end{aligned} \tag{71}$$

$$\begin{aligned}&+\int_0^\infty \frac{dn_1 dn_2}{2+n_1^2+n_2^2}\\ &\times\left.\left[\int_0^\infty dv e^{-v}\tilde{\phi}\left(\frac{n_1 v}{2},0\right)\tilde{\phi}\left(\frac{n_2 v}{2},0\right)\right]^2\right\} < 0.\end{aligned} \tag{72}$$

This expression for ΔE is finite in the limit $k \to 0$ (see Appendix C for details) and proportional to the squared perturbation strength $[\int_0^\infty du V_{\text{eff}}(u)]^2$. In the limit $\mu \to 1$ (and for sufficiently small λ), we are in the situation where neither $V(z_1)+V(z_2)$ nor U alone creates bound states. Recalling our discussion in Sec. III on the existence of bound states as reflected in the magnitude of variational energy, we conclude from $\Delta E < 0$ that the present approach does predict binding for $\mu = 1$ and for sufficiently small λ. Since the ground state is supposed to be continuous, the very fact of having a negative energy for $\mu = 1$ and not very large λ implies that a bound state will exist for

$$\lambda_c > \lambda > 0, \quad \mu_c < \mu < 1, \tag{73}$$

where neither of the potentials V and U alone allows binding. Here $\lambda_c \geqslant 1$ is some critical value at which the real ground-state energy is equal to $E\{U\}$; recall our discussion in Sec. III. Note that the precise form of $\xi(\rho)$ is irrelevant for the argument. This function has to be normalized and such that the effective potential V_{eff} does not become large for a sufficiently small λ (and, of course, does not vanish for a finite λ). For the rest it can be arbitrary.

Thus in view of (73) we have found an example of so-called *Borromean binding*, where the involved potentials do not produce bound states separately, but their cumulative effects lead to such a state. It is seen from (57) that this unusual type of binding is connected with correlations between the z components of each particle and separately with correlations between their x and y components (which enter via ρ).

Note that for three (or more) interacting pointlike particles (instead of two particles and a surface) this effect was predicted in nuclear physics; see, e.g., Ref. [26] for a review.

VI. NO-BINDING CONDITIONS

A. First method

Here we shall consider certain lower bounds on the sought ground-state energy. Although these bounds are basically algebraic, they are nontrivial, and they allow one to find out under which conditions both adsorption and naturation are absent. In this way we complement the study of the previous section. We employ—with necessary modifications and elaborations for our situation—the method suggested in [27].

Note from (19) that the presence of an infinite wall can be modeled via the boundary condition at the plane $z=0$:

$$\Psi(\vec{r}_1,\vec{r}_2)=0, \quad \text{if } z_1=0 \quad \text{or} \quad z_2=0. \tag{74}$$

Although the physical content of the problem demands that $\Psi(\vec{r}_1,\vec{r}_2)$ be also zero for $z_1<0$ or $z_2<0$, we can formally require only (74) and continue the potential $V(z)$ to $z<0$ via

$$V(-z)=V(|z|). \tag{75}$$

The ground-state energy of the new problem defined with help of (74) and (75) will be obviously equal to the ground state of the original problem.

Let us now introduce a fictive particle with mass M and radius vector

$$\vec{r}_3=(x_3,y_3,z_3). \tag{76}$$

Now Eq. (75) is generalized to the corresponding translation-invariant interaction with the fictive particle:

$$V(|z_k-z_3|), \quad k=1,2. \tag{77}$$

It is again obvious that upon taking the limit $M\to\infty$, the motion of the fictive particle will completely freeze; $\vec{r}_3$ will reduce to a constant which can be taken equal to zero.

Thus the three-particle (two real particles plus the fictive one) Schrödinger equation reads analogously to (14) and (15)

$$\left\{-\frac{1}{2M}\frac{\partial^2}{\partial\vec{r}_3^{\,2}}-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_1^{\,2}}-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_2^{\,2}}+V(|z_1-z_3|)+V(|z_2-z_3|) + U(|\vec{r}_1-\vec{r}_2|)-E(M)\right\}\Psi=0, \tag{78}$$

the correct two-particle energy being recovered in the limit $M\to\infty$.

Note that the boundary conditions (74) are modified as well:

$$\Psi=0, \quad \text{if } z_1=z_3 \quad \text{or} \quad z_2=z_3. \tag{79}$$

It is seen that the Hamiltonian in (78) is invariant with respect to the simultaneous shift of all three radius vectors $\vec{r}_k$ ($k=1,2,3$) by some vector. Since we consider a finite-particle quantum system, symmetry of the Hamiltonian implies symmetry of the corresponding ground-state wave function. Thus we deduce for this function

$$\Psi=\Psi(\vec{r}_1-\vec{r}_2,\vec{r}_1-\vec{r}_3,\vec{r}_2-\vec{r}_3), \tag{80}$$

which implies

$$\left\{\frac{\partial}{\partial\vec{r}_3}+\frac{\partial}{\partial\vec{r}_1}+\frac{\partial}{\partial\vec{r}_2}\right\}\Psi=0. \tag{81}$$

We shall now decompose the Hamiltonian in (78) such that (81) is employed and that the separate sectors of the problem—i.e., surface-particle and interparticle interactions—are made transparent:

$$H\equiv-\frac{1}{2M}\frac{\partial^2}{\partial\vec{r}_3^{\,2}}-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_1^{\,2}}-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_2^{\,2}}+V(|z_1-z_3|)+V(|z_2-z_3|) + U(|\vec{r}_1-\vec{r}_2|) \tag{82}$$

$$=H_0+H_{12}+H_{13}+H_{23}, \tag{83}$$

$$H_0\equiv-\frac{1}{2}\left(\frac{\partial}{\partial\vec{r}_3}+\frac{\partial}{\partial\vec{r}_1}+\frac{\partial}{\partial\vec{r}_2}\right)\left(a\frac{\partial}{\partial\vec{r}_3}+b\frac{\partial}{\partial\vec{r}_1}+b\frac{\partial}{\partial\vec{r}_2}\right), \tag{84}$$

$$H_{13}\equiv-\frac{c}{2}\left(\frac{1}{1+x}\frac{\partial}{\partial\vec{r}_1}-\frac{x}{1+x}\frac{\partial}{\partial\vec{r}_3}\right)^2+V(|z_1-z_3|), \tag{85}$$

$$H_{23}\equiv-\frac{c}{2}\left(\frac{1}{1+x}\frac{\partial}{\partial\vec{r}_2}-\frac{x}{1+x}\frac{\partial}{\partial\vec{r}_3}\right)^2+V(|z_2-z_3|), \tag{86}$$

$$H_{12}\equiv-2d\left(\frac{1}{2}\frac{\partial}{\partial\vec{r}_1}-\frac{1}{2}\frac{\partial}{\partial\vec{r}_2}\right)^2+U(|\vec{r}_1-\vec{r}_2|). \tag{87}$$

The coefficients a, b, c, and d are read off directly from (82)–(87):

$$a=-\frac{2x^2}{(1+2x)^2}, \tag{88}$$

$$c=\frac{(1+x)^2}{(1+2x)^2}, \tag{89}$$

$$b=d=\frac{2x(1+x)}{(1+2x)^2}, \tag{90}$$

where the limit $M\to\infty$ has already been taken. Here x is a free parameter; the boundaries of its change are to be determined below.

Let us now take average of the Hamiltonian H with the ground-state wave function Ψ. The term $\langle\Psi|H_0|\Psi\rangle$ is zero due to (81). We shall now establish when the remaining terms in $\langle\Psi|H|\Psi\rangle$ are certainly positive; that is, when bound—i.e., naturated *or* adsorbed—states are certainly absent.

Changing the variables as

$$\vec{\xi}_1=(1+2x)\vec{r}_1+\vec{r}_3, \quad \vec{\xi}_3=x\vec{r}_1+\vec{r}_3, \tag{91}$$

one reduces H_{13} to a form

$$H_{13}=-\frac{c}{2}\frac{\partial^2}{\partial\vec{\xi}_1^{\,2}}+V(|\xi_{1z}-2\xi_{3z}|), \tag{92}$$

where ξ_{1z} and ξ_{3z} are the third components of the vectors $\vec{\xi}_1$ and $\vec{\xi}_3$, respectively. The constant factor $2\xi_{3z}$ will obviously not change the binding conditions. Recalling boundary conditions (79), we see that $\langle\Psi|H_{13}|\Psi\rangle$ is certainly positive for

$$\mu \leqslant c, \tag{93}$$

where μ is the coupling constant of V, such that H_{13} with $c=1$ has the binding threshold $\mu=1$ [compare with (21) and (52)]. Obviously, $\langle\Psi|H_{23}|\Psi\rangle$ is positive under the same condition (93).

As for $\langle\Psi|H_{12}|\Psi\rangle$, we change the variables as

$$\vec{r}_{12}=\vec{r}_1-\vec{r}_2, \quad \vec{R}_{12}=\frac{\vec{r}_1+\vec{r}_2}{2}, \tag{94}$$

to see that H_{12} takes the form

$$H_{13}=-\frac{2d}{m}\frac{\partial^2}{\partial\vec{r}_{12}^{\,2}}+U(r_{12}). \tag{95}$$

Thus, $\langle\Psi|H_{13}|\Psi\rangle$ is certainly positive for

$$\lambda \leqslant 2d, \tag{96}$$

where λ is the coupling constant of U, such that H_{12} with $2d=1$ has the critical binding threshold $\lambda=1$ [compare with (25) and (45)].

Let us now recall that we employed c and $2d$ as inverse effective masses, which should be positive; thus, we should restrict ourselves to the situations

$$x \geqslant 0 \tag{97}$$

and $x<-1$, as seen from (89) and (90). As inspection shows, the relevant no-binding condition is produced for x changing from zero to plus infinity—i.e., for the branch (97).

Thus, under conditions (93) and (96), where the limit $M\to\infty$ is being taken, the overall bound states are certainly absent.

B. Second method

Let us now turn to another, simpler way of deriving no-binding regions. For some range of parameters, the present method will have a priority over the considered one, and then by combining the two methods we shall get an extended no-binding region. We return to the very original quantum Hamiltonian in (15) and write it as

$$-\frac{\alpha}{4}\left(\frac{\partial}{\partial\vec{r}_1}+\frac{\partial}{\partial\vec{r}_2}\right)^2 \tag{98}$$

$$-\frac{\alpha}{4}\left(\frac{\partial}{\partial\vec{r}_1}-\frac{\partial}{\partial\vec{r}_2}\right)^2+U(|\vec{r}_1-\vec{r}_2|) \tag{99}$$

$$-\frac{1-\alpha}{2}\frac{\partial^2}{\partial\vec{r}_1^{\,2}}+V(\vec{r}_1) \tag{100}$$

$$-\frac{1-\alpha}{2}\frac{\partial^2}{\partial\vec{r}_2^{\,2}}+V(\vec{r}_2), \tag{101}$$

where

$$0 \leqslant \alpha \leqslant 1. \tag{102}$$

The term in (98) is seen to be always positive; for the term (99), we change the variables as in (94), to get that it is always positive for

$$\lambda \leqslant \alpha, \tag{103}$$

while the terms in (100) and (101) are both positive under

$$\mu \leqslant 1-\alpha. \tag{104}$$

Here λ and μ have the same meaning as in (93) and (96). Thus no binding is possible if (103) and (104) are satisfied simultaneously.

C. Convexity argument

As for the last ingredient of our construction, we note that the coupling constants μ and λ enter into Hamiltonian $H(\mu,\lambda)$ in the linear way and that the following convexity feature is valid for the ground state as a function of μ and λ:

$$\min[H(\nu\mu_1+(1-\nu)\mu_2,\nu\lambda_1+(1-\nu)\lambda_2)] \tag{105}$$

$$=\min[\nu H(\mu_1,\lambda_1)+(1-\nu)H(\mu_2,\lambda_2)]$$
$$\geqslant \nu\min[H(\mu_1,\lambda_1)]+(1-\nu)\min[H(\mu_2,\lambda_2)]. \tag{106}$$

In other words, if in the phase diagram the binding—i.e., naturation *or* adsorption—is prohibited at points (μ_1,λ_1) and (μ_2,λ_2)—that is, $\min\,[H(\mu_1,\lambda_1)]\geqslant 0$ and $\min\,[H(\mu_2,\lambda_2)]\geqslant 0$—then there is no binding on the whole line connecting those two points, because from (105) and (106) one has $\min\,[H(\nu\mu_1+(1-\nu)\mu_2,\nu\lambda_1+(1-\nu)\lambda_2)]\geqslant 0$.

Thus we draw together the bounds (93), (96), (103), and (104)—under conditions (97) and (102) determining the ranges of the parameters x and α, respectively—and complete it to a convex figure ensuring that for every two points belonging to (93), (96), (103), and (104) the line joining them is also considered as binding prohibited. The result is presented in Fig. 1. It is seen that there is the critical strength $\mu_c=0.25$—which is necessary for binding.

The latter value of μ is special for the following reason: for $\lambda\to\infty$—i.e., when the interparticle attraction is too strong—the two particles are tightly connected to each other. The mass of the composite particle is 2 times larger, and (at the same time) the potential acting on it is 2 times larger. This leads to the adsorption threshold $\mu=0.25$, which is independently obtained via the above no-binding conditions.

VII. PHASE DIAGRAM

We are now prepared to present in Fig. 1 the qualitative phase diagram of the model. The axes of the phase diagram are λ and μ. The dimensionless parameter λ enters into the interstrand interaction energy $\lambda\tilde{U}$, such that without the adsorbing surface the naturated phase of the two strands exists only for $\lambda\geqslant 1$; see Secs. II B and II C for details. In this phase the two strands are localized next to each other and their fluctuations are correlated. The typical form of λ for the considered short-range potentials is

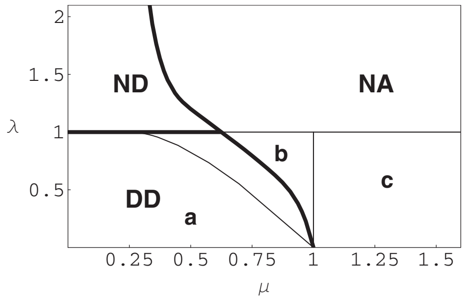

FIG. 1. Schematic phase diagram for the interstrand coupling λ versus the strand-surface coupling μ. The bold lines confine three thermodynamical phases. ND: naturation and desorption. NA: naturation and adsorption. DD: desorption and denaturation. The critical naturation strength in the bulk is $\lambda_c=1$; for single strand adsorption, it is $\mu_c=1$. The following subregions are confined by normal lines. *a*: domain described by the no-binding condition of Sec. VI. *b* (bounded by the bold DD-NA line and two straight segments): Borromean naturation and adsorption. *c*: adsorption and naturation due to overcritical coupling to the surface.

$$\lambda = \frac{c\nu}{a^2 l_p^2 T}, \tag{107}$$

where c is a numerical prefactor, ν is the strength of the interstrand potential (i.e., the modulus of its minimal value), l_p is the persistence length, and T is temperature (recall that Boltzmann's constant is unity, $k_B=1$); see Sec. II B for mode details. In particular, recall that for the Morse potential discussed around Eq. (26) the concrete formula for λ reads $\lambda = \frac{16\nu}{a^2 l_p^2 T}$, where $\nu \simeq 0.01$ eV, $l_p \simeq 1$ nm, and $al_p \simeq 2$ [7]. Taking room temperature for T, we get that $\lambda \sim 1$.

Analogously, the dimensionless parameter μ enters the strand-surface attractive potential as $\mu\tilde{V}$, such that the adsorbed phase of one single strand (that is, without interstrand interaction) exists for $\mu \geqslant 1$; see Secs. II A and II C for details. Note that μ has the same qualitative form (107), where ν is the strength of the surface-strand potential. Recall that for the electrostatic surface-monomer attraction the concrete expression for μ is discussed in (22): $\mu = \frac{8.33\pi|\sigma q|}{T k_D^3 l_p^2 \epsilon}$, where k_D^{-1} is the Debye screening length ($k_D^{-1}=0.1$ nm at normal conditions), q is the monomer charge (around one electron charge for single-strand DNA), l_p is the persistence length (around 1 nm for single-strand DNA), and finally σ is the charge density of the surface. Strongly charged surfaces have typically 1–10 electron charges per 1 nm^2. At room temperature, $\mu \sim 1$.

In Fig. 1 the thermodynamical phases are confined by thick lines. ND, NA, and DD refer, respectively, to the naturated-desorbed, naturated-adsorbed, and denatured-desorbed phases. The meaning of these term should be self-explanatory; e.g., in the ND phase, the two strands are localized next to each other, but they are far from the surface.

First of all, we see that there is no adsorbed and denaturated phase: as we have shown already in Sec. IV, even small (but generic) interstrand (interparticle) attraction suffices to create a naturated state, provided that the two strands (particles) are adsorbed. Thus the rectangular region c in Fig. 1, which belongs to the naturated and adsorbed phase NA, refers to conditions where the overall binding is due to sufficiently strong attraction to the surface.

The curved line going from ($\mu=1$, $\lambda=0$) to ($\mu=0.25$, $\lambda=1$) in Fig. 1 confines region a where no overall binding (i.e., no denaturation and no adsorption) is possible according to the lower bounds obtained in the previous section.

Region b, confined by two straight normal lines and the thick curve, refers to the collective binding situation. It is seen that this region lies below both adsorption and denaturation thresholds. While we do not know the precise position of the thick curve confining region b, we proved its existence in Sec. V.

Finally, the line separating the NA (naturated-adsorbed) phase from the ND (naturated-desorbed) phase extends monotonically to $\mu=0.25$ for $\lambda \to \infty$. Note that the monotonicity of this line is conjectured. Still this conjecture is, to our opinion, quite likely to be correct.

VIII. SUMMARY

The main purpose of this paper was in studying DNA denaturation in the presence of an adsorbing plane surface. As we argued in the Introduction, there are several relevant situations when the two processes, adsorption and denaturation, are encountered together. Taking into account the importance of these processes in the physics of DNA, as well as for DNA-based technologies, it is important to understand how specifically adsorption and denaturation interact with each other.

Our two basic findings can be summarized as follows. First, we saw that provided the two strands of DNA are (even weakly) adsorbed on the surface, there is no denaturation phase transition. There is only a smooth crossover from the naturated state to a (very) weakly bound state. Second, we have shown that when the interstrand attraction alone and the surface-strand attraction alone are too weak to create a naturated and adsorbed state, respectively, their combined effect ("Borromean binding") can create such a naturated and adsorbed state.

The results were displayed on a simple model of two coupled homopolymers (strands) interacting with the plane surface. The volume interaction within each homopolymer can be accounted for via renormalizing the persistence length; see Sec. II F. Many realistic features of DNA are thereby put aside; see the beginning of Sec. II. We plan to investigate some of them elsewhere. Another interesting subject is to study the DNA adsorption on a curved surface [28,29].

We nevertheless hope that the basic qualitative aspects of the presented problem are caught adequately and that the presented results increase our understanding of DNA physics.

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APPENDIX A: DERIVATION OF THE SCHRÖDINGER EQUATION FROM A TRANSFER MATRIX

Imposing periodic boundary conditions, the partition function (3) can be written as

$$\mathcal{Z} = \mathrm{Tr}\mathcal{T}^N \equiv \int d\vec{r}_1 d\vec{r}_2 \mathcal{T}^N(\vec{r}_1,\vec{r}_2;\vec{r}_1,\vec{r}_2), \tag{A1}$$

where $\mathcal{T}$ is the transfer operator parametrized with two continuous indices:

$$\mathcal{T}(\vec{r}_1,\vec{r}_2;\vec{r}_1{}',\vec{r}_2{}') = \exp\Big[-\beta[\mathcal{U}(\vec{r}_1-\vec{r}_2)+\mathcal{V}(\vec{r}_1)+\mathcal{V}(\vec{r}_2)] - \frac{\beta K}{2}(\vec{r}_1-\vec{r}_1{}')^2 - \frac{\beta K}{2}(\vec{r}_2-\vec{r}_2{}')^2\Big]. \tag{A2}$$

Thus in the thermodynamic limit $N\to\infty$

$$\mathcal{Z} = \Lambda^N, \tag{A3}$$

where Λ is the largest eigenvalue of $\mathcal{T}$.

For simplicity reasons, the subsequent discussion will be done in terms of a transfer matrix, which depends on a two scalar variables z' and z. The extension to the more general case (A2) is straightforward.

Write the eigenvalue equation for the right eigenvector as

$$\int dz' \, e^{-\beta\mathcal{V}(z)-(\beta K/2)(z-z')^2}\psi(z') = e^{-\beta f}\psi(z), \tag{A4}$$

where $e^{-\beta f}$ and ψ are, respectively, the eigenvalue and eigenvector. It is seen from (A3) that Nf is the free energy of the model in the thermodynamic limit $N \gg 1$ provided that there is a gap between the largest eigenvalue Λ and the one but largest eigenvalue.

One now assumes that

$$\beta K D^2 \gg 1, \tag{A5}$$

where D is the characteristic length of $\psi(z)$. Since $\psi^2(z)$ is the density of monomers, we see that D quantifies the thickness of the adsorbed layer. Recalling (4) we can write condition (A5) as

$$D \gg l_p; \tag{A6}$$

i.e., the thickness is much larger than the persistence length.

Under condition (A5) the dominant part of the integration in (A4) is $z\approx z'$. With this in mind we expand $\psi(z')$ in (A4) as

$$\psi(z') = \psi(z) + (z-z')\psi'(z) + \frac{(z-z')^2}{2}\psi''(z) + \cdots \tag{A7}$$

and substitute this expansion into (A4). The outcome is

$$\frac{\sqrt{2\pi}}{\sqrt{K\beta}} e^{-\beta\mathcal{V}(z)}\left(1+\frac{1}{2\beta K}\frac{d^2}{dz^2}\right)\psi(z) = e^{-\beta f}\psi(z). \tag{A8}$$

The corrections to this equation are of order $O(\frac{1}{K^2\beta^2D^4}) = O(\frac{l_p^4}{D^4})$.

Equation (A8) can be rewritten as

$$\frac{1}{2\beta K}\frac{d^2}{dz^2}\psi(z) = [e^{\beta[\mathcal{V}(z)-\tilde{f}]}-1]\psi(z), \quad \tilde{f} \equiv f + \frac{T}{2}\ln\frac{2\pi}{K\beta}. \tag{A9}$$

For weakly bound states,

$$|\mathcal{V}(z)-\tilde{f}| \ll 1, \tag{A10}$$

for those z where $|\psi(z)|$ is sufficiently far from zero. Thus in (A9) we can expand

$$e^{\beta[\mathcal{V}(z)-\tilde{f}]} - 1 \simeq \beta[\mathcal{V}(z)-\tilde{f}] \tag{A11}$$

and get the Schrödinger equation:

$$\left(-\frac{1}{2}\frac{d^2}{dz^2} + \beta^2 K \mathcal{V}(z)\right)\psi(z) = \left(\beta^2 K f + \frac{\beta K}{2}\ln\frac{2\pi}{\beta K}\right)\psi(z) \equiv E\psi(z). \tag{A12}$$

The ground-state energy E of this Schrödinger equation relates to the free energy f of the original polymer problem. For weakly bound states, E is negative and close to zero.

APPENDIX B: SOLUTION OF THE SCHRÖDINGER EQUATION WITH THE δ-SHELL POTENTIAL

1. Discrete spectrum

Here we outline bound-state solutions of a one-dimensional Schrödinger equation

$$-\frac{1}{2m}\psi''(x) + [V(x)-E]\psi(x) = 0, \tag{B1}$$

with the attractive δ-shell potential[5]

$$V(x) = -\frac{\mu}{2mx_0}\delta(x-x_0) \tag{B2}$$

and with the infinite wall at $x=0$:

---

[5] We should like to clarify the physical meaning of studying the δ-shell potential (B2). First of all, it should be clear that the weak-potential condition (A11) does not (formally) hold for the strongly singular potential (B2). Thus the transition from the transfer-matrix equation to the Schrödinger equation is *formally* not legitimate. Nevertheless, there is a clear reason for studying the potential (B2) in the context of polymer physics, since it is known that the physics of weakly bound quantum particles in a short-range binding potential does not depend on details of this potential [22]. So once the conditions for going from the transfer-matrix equation to the Schrödinger equation are satisfied for some short-range potential, one can employ the singular potential (B2) for modeling features of weakly bound particles in that potential. This is in fact the standard idea of using singular potentials.

$$\psi(0) = 0. \tag{B3}$$

Here $\lambda > 0$ is the dimensionless strength of the potential, while x_0 is the radius of attraction. m is the particle mass. In contrast to the main text, here we do not put $m=1$.

Due to boundary condition (B3), the considered problem is equivalent to the corresponding three-dimensional Schrödinger problem with centrally symmetric potential.

Let us rewrite (B1) as

$$\psi''(x) - k^2\psi(x) = -\frac{\mu}{x_0}\delta(x-x_0)\psi, \quad k \equiv \sqrt{2m|E|} \geqslant 0. \tag{B4}$$

For $x \neq x_0$, Eq. (B4) is a free wave equation. Its solutions for $x < x_0$ and $x > x_0$ are found from the boundary conditions $\psi(x=0)=0$ and $\psi(x\to\infty)=0$, respectively. Thus the overall solution is obtained as

$$\psi(x) = \mathcal{N}^{-1/2}\sinh(kx_<)e^{-kx_>}, \tag{B5}$$

$$x_< \equiv \min(x,x_0), \quad x_> \equiv \max(x,x_0), \tag{B6}$$

where $\mathcal{N}$ is the normalization constant determined via $\int_0^\infty dx\psi^2(x)=1$,

$$\mathcal{N} = \frac{e^{-2kx_0}}{4k}[\sinh(2kx_0) - 2kx_0] + \frac{\sinh^2(kx_0)}{2k}e^{-2kx_0}. \tag{B7}$$

Substituting (B5) into (B4) we get an equation for the energy of the single bound state:

$$kx_0 = \mu\sinh(kx_0)e^{-kx_0}. \tag{B8}$$

The critical strength of the potential is seen to be

$$\mu = 1, \tag{B9}$$

because, for small kx_0, Eq. (B8) gives

$$kx_0 = \frac{\mu - 1}{\mu}. \tag{B10}$$

Note the following form of $\psi(x)$ for small values of kx_0:

$$\psi(x) = \frac{\sqrt{2k}x_<}{x_0}e^{-k(x_> - x_0)} + O(k). \tag{B11}$$

For large values of λ the bound-state energy increases as

$$2kx_0 = \mu. \tag{B12}$$

2. Continuous spectrum

For studying the continuous (positive-energy) spectrum of Eq. (B1), we rewrite it as

$$\tilde{\psi}''(x) + n^2\tilde{\psi}(x) = -\frac{\mu}{x_0}\delta(x-x_0)\tilde{\psi}, \quad n \equiv \sqrt{2mE} \geqslant 0. \tag{B13}$$

The solution is found as

$$\tilde{\psi}(nx,n) = \frac{\sqrt{2}}{\sqrt{\pi}\sin(nx_0)}\sin(nx_<)\sin[nx_> + \delta(n)], \tag{B14}$$

where $\delta(n)$ is the phase shift to be determined below and where $\tilde{\mathcal{N}}$ is the normalization constant determined via orthogonalization on the n scale:

$$\int_0^\infty dx\tilde{\psi}(nx,n)\tilde{\psi}(nx,n') = \delta(n-n'). \tag{B15}$$

This normalization can be checked via the large-x behavior of $\tilde{\psi}(x,n)$ [22]. Note that for $\tilde{\psi}(nx,n)$ there are two types of dependence on the wave number n: as a prefactor for the argument and as a parameter entering into the normalization and the phase shift.

For the phase shift $\delta(n)$ we get

$$nx_0\sin\delta(n) = \mu\sin(nx_0)\sin[nx_0 + \delta(n)], \tag{B16}$$

which for $n \to 0$ reduces to

$$\frac{1}{\mu} - 1 = \frac{nx_0}{2}\cot[\delta(n)]. \tag{B17}$$

Thus

$$\delta(0) = 0, \tag{B18}$$

and for $\tilde{\psi}(nx,0)$ we have

$$\tilde{\psi}(nx,0) = \frac{\sqrt{2}x_<}{\sqrt{\pi x_0}}\sin(nx_>). \tag{B19}$$

APPENDIX C

While the finiteness of the integral (71) is obvious [because the integral $\int_0^\infty dn/(1+n^2)$ is already convergent], the convergence of the integral in (72) is less trivial. Estimating from (B14) and (B19),

$$\tilde{\phi}(nx,0) = \sqrt{\frac{2}{\pi}}\sin(nx), \tag{C1}$$

we get for the integral in (72)

$$\frac{4}{\pi^2}\int_0^\infty \frac{dn_1 dn_2}{\frac{1}{2} + n_1^2 + n_2^2}\frac{n_1^2 n_2^2}{[(n_1^2 - n_2^2)^2 + 2(n_1^2 + n_2^2) + 1]^2}$$

$$= \frac{1}{4\pi^2}\int_0^{2\pi}\int_0^\infty \frac{d\alpha n dn}{\frac{1}{2} + n^2}\frac{n^4\sin^2 2\alpha}{[n^4\cos^2 2\alpha + 2n^2 + 1]^2} \tag{C2}$$

$$= \frac{1}{4\pi^2}\int_0^{\pi}\int_0^\infty \frac{d\alpha dn}{\frac{1}{2} + n}\frac{n^2\sin^2\alpha}{[n^2\cos^2\alpha + 2n + 1]^2}. \tag{C3}$$

The integral over n in (C3) is convergent and produces an integrable logarithmic singularity $\sim \ln\cos^2\alpha$. Thus the double integral in (C3) is finite.

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