I. INTRODUCTION

A dramatic progress has been made over last decade in employing the single-molecule micromanipulation techniques for studies of biological materials and processes. Pioneered by the work of Smith et. al. [1] on stretching of double-stranded DNA (dsDNA), these techniques have later been applied to study proteins, DNA–protein interactions, chromosomes etc. The chain–stretching experiments were also performed on single–stranded DNA (ssDNA)[2]–[5].

One could expect the response of ssDNA to stretching to be dramatically different from that of dsDNA, because of the effects of the possible basepairing between complementary segments of the chain. The need for understanding of the resulting mechanical behavior has already attracted a considerable attention of theorists [6]-[10]. In particular, it has been shown [7]-[9] that in the thermodynamic limit, ssDNA chain should undergo the second–order phase transition, and a sharp crossover, reminiscent of the first-order “unzipping” transition in dsDNA. We apply the theory to the particular cases of Worm-like Chain (WLC) and Freely-Joint Chain (FJC) models, and discuss the universal and model–dependent features of the mechanical response of ssDNA. In particular, we show that variation of the width of the unzipping crossover with interaction strength is very sensitive to the energetics of hairpin loops. This opens a new way of testing the elastic properties of ssDNA.

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II. THEORETICAL FRAMEWORK

We consider ssDNA chain subjected to external pulling force \( f \). As an input for our theory, one has to specify two functions characterizing the system without self–interactions: \( q_\text{el}(f) \) – elastic free energy per unit chain length vs. pulling force; and \( F_{\text{loop}}(l) \) – free energy of a loop as a function of its contour length. Our goal is to study the effect of interactions between complementary segments of the chain. Similarly to ref [7], we assume the interaction strength to be the same for any two chain fragments. It will be characterized by a single parameter, \( \epsilon \), defined as pairing energy per unit chain length.
Strictly speaking, this should limit applicability of our approach to self–complementary periodic sequences of ss-DNA (such as ATATAT...). However, as discussed in [7]-[8], this uniform model may be reasonably adequate for random sequences, too. Nevertheless, the effect of randomness remains an important problem for the future studies.

Hybridization of distant chain segments results in looping. Therefore, the interactions reduce the effective (free) chain length \( l \) exposed to the stretching force. Our goal is to calculate the partition function of the system \( Z(L,l) \), parameterized by the total chain length \( L \), and free length \( l \). The general form of the interaction–free partition function is, \( Z_0(L,l) \equiv \exp(\mu_0L)\delta(L-l) \), because \( l \) and \( L \) coincide, and different chain segments are statistically independent (we neglect excluded volume effects). Without loss of generality, one can choose \( \mu_0 = 0 \). It is useful to perform double Laplace transform of partition function \( Z(L,l) \). This results in introduction of parameters \( \mu \) and \( q \), conjugated to \( L \) and \( l \) respectively (parameter \( \mu \) conjugated to the total length, is often called fugacity):

\[
Z(\mu, q) = \int_0^{+\infty} \int_0^{+\infty} Z(L,l) \exp[-\mu L - q l] \, dL \, dl. \tag{1}
\]

In particular, \( Z_0(\mu, q) = 1/(\mu + q) \). Since the elastic part of free energy is \( q_{el}(f)l \), the overall free energy may be expressed as

\[
F(L,f) = -\log \int_{-\infty}^{+\infty} Z(\mu, q_{el}(f)) e^{\mu L} d\mu. \tag{2}
\]

Here and below, we take \( k_B T = 1 \).

It is well known that the partition function of a uniform RNA or ssDNA may be calculated in a recursive manner, reminiscent of Hartree approximation [6]-[11]. This calculation can be represented in a diagrammatic form shown in Figure 1. The solid lines correspond to bare partition function \( Z_0 \); dotted fragments connected with dashed lines represent pairing (hybridization) of the corresponding chain segments. Within our approach, the energy cost of the pairing is \( \epsilon L_{hyb} + F_{loop}(l) \), where \( L_{hyb} \) is the length of the hybridized region, and \( l \) is the free length of the chain segment being "internalized" due to the looping. In fact, one can extend our approach to a more general form of hybridization energy, \( \epsilon_0 + \epsilon L_{hyb} \), with constant \( \epsilon_0 > 0 \) representing the energy cost of termination of the double–stranded segment. Introduction of \( \epsilon_0 \) accounts for the cooperativity of the basepairing interactions.

Traditionally, problems involving DNA/RNA folding or denaturation, are studied within a discreet model. Each discrete "monomer" in this approach represents a chain segment which can hybridize independently of its neighbors. Its length is assumed to be equal to the statistical segment, which makes it easy to combine this description with FJC model. Since we are interested in developing a theory for an arbitrary model of chain elasticity, it is logical to abandon this artificial discretization of hybridized segments. Of course, the basepairing remains fundamentally discreet on the length scale \( l_0 \) of a single base. As long as the relevant physics occurs on larger scales, ssDNA can be considered as a continuous chain.

The crucial observation is that one can typically neglect all the diagrams with intersecting dashed lines. Such situation would correspond to "pseudo–knot", whose probability is low because it requires winding of ss-DNA/RNA around itself (Fig. 1b). Thanks to this topological constrain, "self energy" diagram entering Dyson equation (Fig 1c), may be calculated exactly within one-loop (Hartree) approximation. Since we have assumed the uniform interaction parameter, the problem has a particularly simple form at the Laplace representation:

\[
Z^{-1}(\mu, q) = Z_0^{-1}(\mu, q) - \iint \frac{dL'dL''}{l_0^3} Z(L',l) \times \exp[-\mu (2L'' + L') - \epsilon L'' - F_{loop}(l) - \epsilon_0]. \tag{3}
\]

From here, one can obtain:

\[
Z^{-1}(\mu, q) = \mu + q - \frac{W(q_\mu)}{2\mu + \epsilon}, \tag{4}
\]

were \( q_\mu \) corresponds to the pole in \( Z(\mu, q) \), and

\[
W(q) = e^{-\epsilon_0} \int_0^{+\infty} \exp[-F_{loop}(l) + q l] \, dl. \tag{5}
\]

III. GENERIC BEHAVIOR: "UNZIPPING" VERSUS "UNFOLDING"
In the thermodynamic limit \((L \rightarrow \infty)\),
\[
    l = -\frac{\partial}{\partial q} \log \left[ \int_{-i\infty}^{+i\infty} Z(\mu, q) e^{i\mu t} \frac{d\mu}{2\pi i} \right]_{q_{el}(f)} = -L \frac{d\mu_q}{dq} \bigg|_{q_{el}(f)}.
\]
(6)

Here function \(\mu_q(q)\) again corresponds to the pole in \(Z(\mu, q)\), i.e. it is inverse to \(q_{el}(\mu)\). Explicitly,
\[
    \mu_q(q) = -\frac{1}{2} \left( \frac{\epsilon}{2} + q - \sqrt{\left( \frac{\epsilon}{2} - q \right)^2 + 2W(q)} \right). \tag{7}
\]

This yields the following result for the free length as a function of tension:
\[
    \frac{l}{L} = \frac{1}{2} \left( 1 - \frac{q_{el} - \epsilon/2 + W'(q_{el})}{\sqrt{(q_{el} - \epsilon/2)^2 + 2W(q_{el})}} \right). \tag{8}
\]

Here \(W' \equiv dW/dq\). Note that from the definition of function \(W\), Eq. (5), one can relate its logarithmic derivative to the average length of the loop:
\[
    l_{\text{loop}}(q) = \frac{W'}{W}. \tag{9}
\]

If \(l\) is known, one can easily find the relative elongation of the chain, i.e. the ratio of the end-to-end distance \(R\) to the total chain length \(L\), which is observable experimentally:
\[
    \frac{R}{L} = xl = -\frac{1}{2} \frac{\partial q_{el}}{\partial f} \left( 1 - \frac{q_{el} - \epsilon/2 + W'(q_{el})}{\sqrt{(q_{el} - \epsilon/2)^2 + 2W(q_{el})}} \right). \tag{10}
\]

Here \(x = -\partial q_{el}/\partial f\) is the relative elongation of the free portion of the chain.

According to Eq. (8), in the strong stretching limit \((q_{el} \rightarrow -\infty)\) the chain becomes completely "free": \(l \rightarrow L\). Further examination of our expression for the free length reveals its peculiar behavior near the point \(q_{el} = \epsilon/2\). In fact, in the limit of vanishing \(W\) (i.e. very high energy cost of a loop), \(l(q_{el})\) becomes a step function changing from 0 to \(L\) at that point. In a realistic situation, it is transformed into a crossover whose width depends on \(W\), as
\[
    \delta_q = \sqrt{2W(\epsilon/2)}. \tag{11}
\]

Since the location of that crossover corresponds to the point where the hybridization free energy is exactly equal to the elastic one, we conclude that this behavior is directly related to the first-order unzipping transition of dsDNA. The transition is transformed into the crossover due to the finite size of the hybridized segments.

Another important feature of our result is that the free fraction of the chain \(l/L\) goes to zero at finite tension \(q_{el} = q^*\). According to Eq. (8) the condition for this to happen is,
\[
    q^* - \epsilon/2 = \frac{W'(q^*)}{W'(q^*)} - \frac{2}{W'(q^*)} = \frac{1}{l_{\text{loop}}(q^*)} - \frac{l_{\text{loop}}(q^*)^2}{l_0^2} W(q^*) \tag{12}
\]

This point corresponds to the second order phase transition, which has been reported in the earlier studies of the problem. The crucial observation is that this transition is physically distinct from the unzipping crossover. It may be viewed as a precursor of the force-induced denaturation. Indeed, even when the tension in the free segments is still insufficient to overcome the binding energy \(-\epsilon\), one can convert a finite fraction of the chain into the free length without breaking any bonds. Namely, since there is a finite density of loops at the folded ssDNA, one can simply "move" the unbound bases from the loops to the free segment. This will only result in an entropy loss, but will not reduce the interaction energy.

Indeed, if the basepairing energy is negative, the magnitude of the critical tension is somewhat lower \((|q^*| < -\epsilon/2)\) than that at the unzipping point:
\[
    \frac{q^* - \epsilon}{2} \approx \frac{1}{l_{\text{loop}}(q^*)}. \tag{13}
\]

The free segments of the chain exposed to the external stretching can be viewed as topologically distinct objects ("vortices"), which separates the system onto independently folded domains. The effective interaction potential of two consequent vortices is determined by the free energy of the folded region between them. At the point \(q^*\), the typical separation between the vortices along the chain coordinate, i.e. the size of the separable domains, diverges. This folding-unfolding transition occurs as a result of competition between the elastic tension and folding entropy, which grows with the domain size.

Interestingly, Eq. (12) has physical solutions even for positive interaction energy, i.e. when the basepairing is energetically unfavorable. It follows form the fact that for \(l_{\text{loop}} \rightarrow \infty\), the generic behavior of looping free energy is \(F_{\text{loop}}(l) \approx 3/2 \log l\), (for an ideal Gaussian chain). As a result, \(W(q)\) remains finite for \(q \rightarrow 0\) , while \(W'\) and \(l_{\text{loop}}(q^*)\) are diverging, as \(q^* - 2\). Therefore, according to Eq. (12), there is a finite tension at which the unfolding transition takes place, for \(\epsilon > 0\). The asymptotic relationship between \(\epsilon\) and \(q^*\) in this regime is,
\[
    l_{\text{loop}}(q^*) \approx \frac{\epsilon^2}{2} W(0) \tag{14}
\]

This yields a power law dependence of the critical tension on \(\epsilon\): \(q^* \sim \epsilon^{-2}\). Note however that our conclusion about the unfolding transition at positive values of basepairing energy, may well be a result of limitations of the model.
IV. APPLICATION TO WORM-LIKE CHAIN MODEL

As an example, we discuss the application of the above approach to the particular case of WLC model. Its Hamiltonian is given by

$$H = \int_0^L \left[ \frac{l_p}{2} \left( \frac{\partial^2 r}{\partial s^2} \right)^2 \right] ds$$  \hspace{1cm} (15)

were $l_p$ is persistence length, and $r(s)$ defines the spatial conformation of the chain, subjected to constrain $|\partial r/\partial s| = 1$. For this model, Marko and Siggia [17] have proposed the following interpolative relationship between the stretching force $f$ and relative extension $x \equiv R/L$.

$$f(x) = \frac{1}{l_p} \left( \frac{1}{4} \left[ \frac{1}{(1-x)^2 - 1} \right] + x \right)$$  \hspace{1cm} (16)

From here, function $q_{cl}(f)$ (which is one of the inputs for our theory), can be expressed in parametric form:

$$q_{cl}(f) = \int_0^x f(x') dx' - xf(x) = -\frac{x^2}{4l_p} \left[ \frac{1}{(1-x)^2} + 2 \right]$$  \hspace{1cm} (17)

One has also to specify the loop free energy. An analytic interpolation for $F_{\text{loop}}$ was proposed in Ref. [19], in the context of the ring cyclization problem:

$$e^{-F_{\text{loop}}} \approx \frac{v_0}{l_p^3} \begin{cases} 4\pi^3 \left( \frac{2\pi l_p}{l} \right)^6 \exp \left( -\frac{2\pi^2 l_p}{l} + \frac{l}{4l_p} \right), & l < 4l_p \\ \left( \frac{3}{\pi l_p} \right)^{3/2} \left[ 1 - \frac{1}{l/l_p} + \frac{l^2}{l_p^2} \right], & l > 4l_p \end{cases}$$  \hspace{1cm} (18)

Here $v_0 \lesssim 1A^3$ is the effective "reaction volume" associated with the localization of the loop ends by the hydrogen bonding. We have found a simpler version of the interpolative expression, which gives a very good fit to the global behavior of the looping probability, $e^{-F_{\text{loop}}}$ (see Figure 2):

$$e^{-F_{\text{loop}}} \approx v_0 \left( \frac{3}{\pi l_p (l-l_p)} \right)^{3/2} \exp \left( -\frac{4.5}{l/l_p - 1} \theta (l-l_p) \right)$$  \hspace{1cm} (19)

Here $\theta$ is the step function.

Within this approximation, function $W_{\text{WLC}}(q)$ can be found analytically:

$$W(q) \approx \frac{\alpha}{l_p^2} \exp \left[ -3\sqrt{2q} l_p + q l_p \right]$$  \hspace{1cm} (20)

Here

$$\alpha = \frac{\sqrt{6} v_0}{\pi l_p^2} e^{-\varepsilon_0}$$  \hspace{1cm} (21)

Note that $\alpha$ replaces three parameters of the original model, $v_0$, $l_0$, and energy $\varepsilon_0$. Since $\delta \lesssim l_0$, and $\varepsilon_0 > 0$, this dimensionless parameter is expected to be small. It has a physical meaning of the effective reaction volume of the loop ends, in units of $l_p^3$.

Now that we have specified $W_{\text{WLC}}(q)$ and $q(f)$, Eqs. (6)-(7), can be used to find $l(f)$, together with force–extension curves, $R(f) = l(f)x(f)$. The fact that $\alpha$ is a small parameter allows us to simplify the results. In the regime of negative $\epsilon$, a sharp unzipping crossover is expected. As we have discussed in the previous section, its characteristic width is given by

$$\delta_q = \sqrt{2W(\epsilon/2)} = \sqrt{\frac{2\alpha}{l_p^3}} \exp \left[ \left( -6\sqrt{-\epsilon l_p} + l_p \right)/4 \right]$$  \hspace{1cm} (22)

In the vicinity of the crossover point, $q_{cl} = \epsilon/2$, the change in free length can be well described by the universal function of rescaled variable $\Delta = (q - \epsilon/2)/\delta_q$:

$$\frac{l}{L} \approx \frac{1}{2} \left( 1 - \frac{\Delta}{\sqrt{\Delta^2 + 1}} \right)$$  \hspace{1cm} (23)

For large enough $\Delta$, this universal behavior breaks down due to the proximity of the unfolding phase transition. The corresponding critical tension $q^*$ is given by:

$$q^*_{\text{WLC}} \approx \frac{\epsilon}{2} + \frac{1}{l_{\text{loop}}(\epsilon/2)} \approx \frac{\epsilon}{2} + \frac{1}{l_p (1 + 3/\sqrt{-\epsilon l_p})}$$  \hspace{1cm} (24)

Figure 3 shows the sharp crossover at $|q(f)| = \epsilon/2$. Consistently with Eq. (22), its sharpness increases with lowering parameter $\alpha$. This can be associated with growth of the typical length of hybridized regions. The unzipping is clearly separated from second–order unfolding transition. While this crossover regime was not...
present at the early studies of the problem, it has been recently reported in Ref. [9]. In that work, the traditional FJC-based model has been modified to include the effects of cooperativity, analogous to our parameter $\varepsilon_0$. As we have discussed, the sharp crossover should be interpreted as unzipping (force induced denaturation), while the second-order transition corresponds to topological change (unfolding) which may be viewed as a precursor of the unzipping. This physical picture is consistent with the results of Ref. [9]. On the other hand, our analysis disagrees with the conclusions of Ref. [10], in which the first order phase transition was predicted for the regime of strong enough hybridization energy.

V. MODEL DEPENDENCE OF THE RESULTS

Here we discuss how the above results may depend on the choice of the elastic description of ssDNA. It should be noted that such important features, as the unfolding transition and the unzipping crossover, are very robust and nearly independent of the model. Furthermore, it is well known the stretching curve of ssDNA may be fitted reasonably well by several models, e.g. extensible versions of FJC, WLC, or DPC. This implies that deduction of $q_{cl}(\epsilon)$ from the existing and future experimental data is unlikely to provide a sensitive test for the possible models. On the other hand, we have seen that the loop free energy $F_{loop}(l)$ and consequently $W(q)$ are significant parameters of the problem. As we shall see, this parameters are very sensitive to the choice of the underlying elastic model.

In the case of Discreet Persistent Chain (DPC) model, we do not expect any significant deviation of $F_{loop}(l)$ or $W(q)$ from those obtained for WLC model, since the typical bending radius significantly exceeds the bond length. The (extensible) FJC model has been a standard framework in which the discussed problem has been studied so far. Nevertheless, here we briefly review the results of our theory for FJC, in order to identify the major model-dependent features. The freely joint chain consists of discreet bonds of length $a = 2l_p$, whose orientations are mutually independent. The corresponding loop free energy can be written as,

$$\exp [-F_{loop}(l)] \simeq 2 \left( \frac{3}{2\pi} \right)^{3/2} \frac{\varepsilon_0}{l_p^2} \sum_{n=1}^{\infty} \frac{\delta (l - 2n\ell_p)}{n^{3/2}} \tag{25}$$

The prefactor here ensures that the asymptotic behavior of the free energy at the large-loops limit coincides with the WLC result, given by Eq. (18). Now, one can find $W(q)$ for FJC model:

$$W(q) = \frac{3\alpha}{2\sqrt{\pi l_p^2}} \sum_{n=1}^{\infty} \exp \left( 2qnl_p \right) n^{3/2} \tag{26}$$

For negative $\epsilon$, the change of the elastic description results in a modest shift of the critical tension $q^*$ at which the unfolding transition occurs:

$$q_{FJC}^* \simeq \frac{\epsilon}{2} + \frac{1}{l_p^2 \epsilon / 2} \simeq \frac{\epsilon}{2} + \frac{1}{2l_p^2} \tag{27}$$

This should be compared to WLC result, Eq. (24). While the position of the unzipping point, $q_{cl} = \epsilon/2$, is model independent, the width of the crossover is very sensitive to the behavior of $W(q)$. As one can see in Figure 4, the shapes of $W(q)$ curves are substantially different for WLC and FJC models. This difference arises because of the relative suppression of the short loops in WLC case. What is especially remarkable is that the width of the unzipping crossover, $\delta_q = \sqrt{2W(\epsilon/2)}$, decreases with $\epsilon$ in a strongly model dependent manner. In fact, upon change of $\ell_p$ from 0 (dsDNA denaturation point) to $3kT$ (which roughly corresponds to physiological conditions for GCGCGC– sequence), the ratio of $\delta_q$ for the two models changes by factor of $\approx 3.5$. Therefore, an experimental study of the unzipping crossover at variable conditions (e.g. temperature), would open a new possibility of testing the plausible models of ssDNA elasticity.

VI. CONCLUSIONS

In this paper, we have discussed the effects of basepairing on the stretching behavior of ssDNA, within a theoretical framework compatible with an arbitrary underlying model of chain elasticity. Our conclusion is that in a generic case, the stretching curves exhibits two related but distinct feature: the second-order unfolding phase transition, and the sharp unzipping crossover. The latter is reminiscent of the first–order transition in dsDNA,
as well as to the mechanical response of non-random RNA molecules\[6\]. On the other hand, we have interpret the unfolding as a topological transition. At the critical point, the typical size of independently folded domains diverges (in the thermodynamic limit). This transition is due to the competition of conformational entropy and elastic free energy, and it is expected to occur even in the regime when basepairing is energetically unfavorable.

In the light of our results, one can see a clear relationship between the three types of the force-induced denaturation: (i) unzipping of dsDNA\[13\]-[14], (ii) denaturation of RNA with a preferred secondary structure\[6\], and (iii) stretching a self–complimentary or random ssDNA. While in the case of dsDNA the unzipping occurs as a first order transition, it becomes a crossover for the two other cases. The width of the crossover is defined by the typical length of a single hybridized region. We expect this width to be sensitive to the sequence of ssDNA/RNA. In fact, the force-induced denaturation of RNA \[6\] was predicted to show a sequence of unzipping steps. It follows from our discussion that the sharpness of those steps may be even more pronounced than was originally predicted within FJC-based model. In the case of ssDNA, the sequence disorder must result in smearing of the unzipping crossover. Because of its entropic nature, the unfolding transition is expected only in the case of ssDNA (or long RNA, in molten phase \[11\]).

At present, the experimental indications of the second order unfolding transition are not conclusive enough \[3\]-\[4\]. On the other hand, experiments with uniform self–complimentary DNA show a clear manifestation of the sharp unzipping crossover \[5\]. However, their precision is still insufficient to make a quantitative comparison with the theory, and to distinguish between different underlying elastic models. Based on our theory, one may extract this information by performing a systematic experimental study of the unzipping behavior for various values of hybridization energy (e.g. various temperatures). As we have shown, the width of the crossover is very sensitive to the energy cost of the hairpin loop.

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