

Stretching semiflexible filaments with quenched disorder

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We study the effect of quenched randomness in the arc-length dependent spontaneous curvature of a wormlike chain under tension. In the weakly bending approximation in two dimensions, we obtain analytic results for the force-elongation curve and the width of transverse fluctuations. We compare quenched and annealed disorder and conclude that the former cannot always be reduced to a simple change in the stiffness of the pure system. We also discuss the effect of a random transverse force on the stretching response of a wormlike chain without spontaneous curvature.

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I. INTRODUCTION

The wormlike chain (WLC) model of semiflexible polymers treats the macromolecules as one-dimensional locally inextensible curves with bending rigidity [1–5]. Despite its simplicity and its initial success with the experiments on stretching of ds-DNA [6], the inherent complexity in the microscopic architecture of biological filaments invites the search for more realistic models. One key feature of many biopolymers, such as DNA or denatured proteins, which goes beyond the classical WLC is their heterogeneity. Their local architecture (e.g., spontaneous curvature) [7] or their local elasticity (e.g., their bending rigidity) vary along the polymer contour. At large scales, this heterogeneity may statistically behave as a random variable. It may be fixed in time such as that related to the different base pair sequences in DNA. This randomness is treated as quenched disorder. If the random inhomogeneity undergoes thermal fluctuations, it is treated as annealed disorder. An example of the latter is the reversible binding of proteins to DNA capable of inducing spontaneous (intrinsic) curvature which has been studied in [8].

The first studies of the effect of random base pair sequences on the macroscopic statistical properties of DNA focused on the related random bends (spontaneous curvature) and treated them on equal footing as the thermally excited bends, thus considering the annealed disorder case [9–11]. Bensimon *et al.* considered the effect of random angles in the Kartky-Porod chain and using numerical transfer matrix and Monte Carlo methods found that, as far as stretching is concerned, the disordered chain behaves as a homogeneous chain with a renormalized persistence length [12]. Nelson calculated the effect of weak disorder on the entropic elasticity of a flexible rod with random kinks and found that the sole effect was a reduction in the apparent bending stiffness with the twist stiffness remaining unchanged [13]. A different way of modeling disorder has been followed by Debnath and Cherayil [14] who considered the chain under tension as consisting of random A-B blocks with different elastic constants. The blocks were treated as “Gaussian” semiflexible polymers (without the local inextensibility constraint). Muhuri and Rao [15] studied finite size effects in the Kratky-Porod chain with a random sequence of stiffness constants.

In a recent paper [16], we studied the response of a weakly bending WLC with arc-length dependent spontaneous curvature to a stretching force applied at its ends. We specifically considered the case of sinusoidally varying spon-

aneous curvature which allows us to treat the general case via Fourier transformation. This simple and analytically tractable model appears to be particularly well suited for the study of quenched disorder in the spontaneous curvature of a filament under tension. This is the subject of the present paper. A similar calculation with a different method (which is in principle valid) was attempted in Ref. [17], but a mistake in the way the thermodynamic limit was taken led to the incorrect conclusion that sequence disorder has no effect on elasticity. Here, we use the replica trick to calculate the effect of uncorrelated quenched disorder and we obtain the force-extension relationship as well as force-transverse-width relationship. We compare our results with those obtained in the context of annealed disorder. Although, as we show, the two cases (quenched and annealed) are indistinguishable in the limit of weak disorder, our results for quenched disorder hold for arbitrary strength.

We also study the adaptation to the WLC of the classical random-force model which Larkin had introduced in the context of the Abrikosov lattice [18]. As with quenched disorder in the spontaneous curvature in the weakly bending approximation, the coupling of a random force is linear and this makes its analytical treatment straightforward. The effect of quenched random forces on the WLC conformations has recently been analyzed in [19]. Here, we deal with their effect on the stretching response in parallel with our study of the random spontaneous curvature.

II. MODEL

We consider a WLC fluctuating in two dimensions under a strong stretching force applied at its end-points. The restriction for the chain to remain confined to a single plane is made to allow concise analytical treatment. It certainly applies to stretching experiments on a surface [20]. Although it is known the difference between two dimensions (2D) and three dimensions (3D), when the curvature of a freely bending WLC is concerned, to be nontrivial [21], here we stay within the weakly bending approximation where it can be shown, using the Monge gauge [22], that the two transverse directions of a (1+2)-dimensional chain decouple. Our recovery, for a special case of disorder, of the main result of Ref. [13] which was based on a 3D model further attests to the validity of the main features of our results beyond 2D. Quenched disorder along the polymer contour is represented

by a random distribution of the arc-length dependent spontaneous curvature. The strong stretching force allows us to use the weakly bending approximation which significantly simplifies the analytical treatment of the filament response as shown in Ref. [16]. The WLC conformations are parameterized by the displacement $y(s)$, transverse to the direction of the pulling force (x), as a function of the arc-length position s . The elastic energy functional is given by

$$\mathcal{H}_c[y(s)] = \frac{\kappa}{2} \int_0^L ds \left[\left(\frac{\partial^2 y(s)}{\partial s^2} \right) - \bar{c}(s) \right]^2 + \frac{1}{2} f \int_0^L ds \left(\frac{\partial y(s)}{\partial s} \right)^2 - fL, \quad (1)$$

where κ is the bending rigidity related to the persistence length via $\kappa = \frac{1}{2} L_p k_B T$, f is the applied stretching force, L is the total contour length, and $\bar{c}(s)$ is the signed spontaneous curvature. The probability distribution of $\bar{c}(s)$ is given by

$$\mathcal{P}[\bar{c}(s)] \sim \exp \left[- \int_0^L ds \frac{1}{2\Delta_c} (\bar{c}(s))^2 \right], \quad (2)$$

and is completely characterized by $\overline{\bar{c}(s)} = 0$ and $\overline{\bar{c}(s)\bar{c}(s')} = \Delta_c \delta(s-s')$, where the overbar denotes an average over the disorder. The delta function reflects the assumption of uncorrelated disorder along the polymer backbone.

Experimentally observable quantities of long polymers with quenched disorder are expected to be self-averaging and are calculated by averaging the free energy over the distribution of disorder [23]. This requires averaging the logarithm of the partition function, a goal which is achieved by employing the standard replica trick [24]. Averaging the partition function itself over disorder corresponds to the annealed system which has been studied in Ref. [17], where it is called the ‘‘disorder-first system.’’

Besides disorder which is related to the spontaneous curvature, in this paper, we also consider the effect of a random transverse force on the force-extension relationship of a WLC without spontaneous curvature. The elastic energy functional of such a system is given by

$$\mathcal{H}_g[y(s)] = \frac{\kappa}{2} \int_0^L ds \left(\frac{\partial^2 y(s)}{\partial s^2} \right)^2 + \int_0^L ds g(s) y(s) + \frac{1}{2} f \int_0^L ds \left(\frac{\partial y(s)}{\partial s} \right)^2 - fL. \quad (3)$$

As usual, the distribution of the random force $\underline{g}(s)$ is assumed to be completely determined by $\overline{g(s)} = 0$ and $\overline{g(s)g(s')} = \Delta_g \delta(s-s')$. The random coupling term in Eq. (3) can be viewed as expressing the interaction of a stretched semiflexible polyampholyte with a quenched linear charge density $g(s)/E$ and a uniform transverse field E . An alternative interpretation of Eq. (3) views $g(s)$ as representing a random interaction with the crowded environment in which the filament fluctuates. Strictly speaking, quenched disorder in the embedding medium (environment) should entail a term $\int_0^L ds g[x(s)] y(s)$, where $x(s) = s - \frac{1}{2} \int_0^s ds' [\partial_{s'} y(s')]^2$, instead of the one written above, but $g(s)$ is expected to capture the leading-order behavior in the weakly bending limit.

III. REPLICA TRICK

The standard method to deal with the quenched disorder average involves averaging over n identical noninteracting copies (replicas) of the system [24]. In the end, the replica limit $n \rightarrow 0$ is taken. The free energy is calculated via $\ln Z = \lim_{n \rightarrow 0} (\overline{Z^n} - 1)/n$, where Z is the partition function of the system with a certain realization of the disorder. $\overline{Z^n}$ can be expressed as $\overline{Z^n} = \exp(-\mathcal{H}^{(rep)}/k_B T)$.

For the random-spontaneous-curvature system described by Eq. (1), the replica ‘‘Hamiltonian’’ takes the form

$$\mathcal{H}_c^{(rep)} = \frac{1}{2} \int_0^L ds \sum_{a=1}^n \left[\kappa \left(\frac{\partial^2 y_a(s)}{\partial s^2} \right)^2 + f \left(\frac{\partial y_a(s)}{\partial s} \right)^2 \right] - \frac{\Delta_c \kappa^2}{2k_B T (1 + n\kappa\Delta_c/k_B T)} \int_0^L ds \sum_{a,b=1}^n \left(\frac{\partial^2 y_a(s)}{\partial s^2} \right) \times \left(\frac{\partial^2 y_b(s)}{\partial s^2} \right), \quad (4)$$

where we have omitted constant terms and the subscripts a, b label the replicas of the original system. In Ref. [16], we have shown that in the strong stretching regime, where $f \gg \kappa/L^2$, the details of the boundary conditions become irrelevant. Therefore we can assume hinged-hinged boundary conditions and a chain with vanishing curvature at its endpoints. In this case, we can use the Fourier decomposition

$$y_a(s) = \sum_{m=1}^{\infty} A_a^{(m)} \sin(q_m s), \quad (5)$$

where $q_m = \pi m/L$ is the wave number of the corresponding m -mode, and express the replica ‘‘Hamiltonian’’ of Eq. (4) in a quadratic matrix form. Correlators can be calculated using the Sherman-Morrison formula from linear algebra. In the replica limit ($n \rightarrow 0$), we get

$$\langle A_a^{(m)} A_b^{(m)} \rangle = \frac{2k_B T}{L q_m^2 (\kappa q_m^2 + f)} \delta_{ab} + \frac{2\Delta_c \kappa^2}{L (\kappa q_m^2 + f)^2} \mathbf{1}_{ab}, \quad (6)$$

where $\mathbf{1}$ is an $n \times n$ matrix with all of its elements equal to 1. Using the matrix determinant lemma and taking the replica limit we also calculate the disorder-averaged free energy and obtain

$$\bar{G}_c = - \frac{k_B T}{2} \sum_{m=1}^{\infty} \left[\ln \left(\frac{\pi}{k_B T (\kappa q_m^2 + f)} \right) - \frac{1}{k_B T (\kappa q_m^2 + f)} \right]. \quad (7)$$

For the random-force system described by Eq. (3), the corresponding replica ‘‘Hamiltonian’’ is given by the analogous procedure,

$$\mathcal{H}_g^{(rep)} = \frac{1}{2} \int_0^L ds \sum_{a=1}^n \left[\kappa \left(\frac{\partial^2 y_a(s)}{\partial s^2} \right)^2 + f \left(\frac{\partial y_a(s)}{\partial s} \right)^2 \right] - \frac{\Delta_g}{2k_B T} \int_0^L ds \sum_{a,b=1}^n y_a(s) y_b(s). \quad (8)$$

Using similar calculations as in the case of random spontaneous curvature, we obtain the correlators

$$\langle A_a^{(m)} A_b^{(m)} \rangle = \frac{2k_B T}{L q_m^2 (\kappa q_m^2 + f)} \delta_{ab} + \frac{2\Delta_g}{L q_m^4 (\kappa q_m^2 + f)^2} \mathbf{1}_{ab}, \quad (9)$$

and the disorder-averaged free energy

$$\bar{G}_g = \frac{k_B T}{2} \sum_{m=1}^{\infty} \left\{ \ln \left[\frac{\pi}{k_B T} (\kappa q_m^2 + f) \right] - \frac{1}{k_B T} \frac{\Delta_g}{q_m^2 (\kappa q_m^2 + f)} \right\}. \quad (10)$$

IV. FORCE-EXTENSION RELATIONSHIP

The average projected length of the filament in the direction of the stretching force is given by

$$\langle x(L) \rangle = L - \frac{1}{2} \int_0^L ds \left\langle \left(\frac{\partial y(s)}{\partial s} \right)^2 \right\rangle, \quad (11)$$

where

$$\left\langle \left(\frac{\partial y(s)}{\partial s} \right)^2 \right\rangle = \frac{1}{2} \sum_{m=1}^{\infty} q_m^2 \overline{\langle (A^{(m)})^2 \rangle} \quad (12)$$

and

$$\overline{\langle (A^{(m)})^2 \rangle} = \lim_{n \rightarrow 0} \frac{1}{n} \sum_{a=1}^n \langle A_a^{(m)} A_a^{(m)} \rangle. \quad (13)$$

In the strong stretching regime, defined by $f \gg f_{cr} \gtrsim f_L$, where $f_{cr} \equiv \kappa/L_p^2$ and $f_L \equiv \kappa/L^2$ (the shorthand notation defining the characteristic force scales), we obtain

$$\frac{\langle x(L) \rangle}{L} - 1 = -\frac{1}{2} \left(\frac{f_{cr}}{f} \right)^{1/2} - \frac{1}{8} \Delta_c L \left(\frac{f_L}{f} \right)^{1/2}. \quad (14)$$

Equation (14) is the central result of our paper. The first term in the right-hand side (rhs) is the well-known expression associated with the ironing out of the thermal undulations [25]. The second term comes from straightening the quenched random undulations related to the spontaneous curvature. This result implies that, as far as the force-extension response is concerned, uncorrelated quenched disorder in the spontaneous curvature acts as an effective linear increase in the temperature given by $k_B \delta T = \kappa \Delta_c / 2$ (using $L_p = 2\kappa/k_B T$). We also point out that for given bending rigidity and disorder strength, the effect of disorder on the force-extension relationship is independent of the polymer size L . This result holds for *arbitrary* strength of disorder, provided that the strong stretching and weakly bending assumptions are fulfilled. Our result does not contradict the claim by Marko and Siggia [25] that disorder related to intrinsic bends with large radius of curvature compared to the persistence length do not alter the large f limit. In fact, *any* arc-length dependent spontaneous curvature whose Fourier spectrum has bounded amplitude does not alter this limit. As we have shown in [16], the response of a weakly bending WLC with arbitrary (but bounded) spontaneous curvature is the superposition of the responses corresponding to sinusoidally varying modes of curvature. The latter contribute terms which scale as $\sim f^{-2}$ and become negligible compared with the thermal term $\sim f^{-1/2}$ as the stretching force increases. The crucial differ-

ence with the case of uncorrelated disorder is that the latter contains bends of unbounded sharpness in a similar fashion as the thermal excitations do. That is the physical reason why the disorder term in Eq. (14) has the same form as the thermal one. Of course, uncorrelated disorder with zero correlation length is a mathematical abstraction. In real systems, there will be a maximum wave number, q_{\max} , in the spectrum of random undulations of the spontaneous curvature. For $f \ll \kappa q_{\max}^2$ [16], disorder approximately behaves as uncorrelated and our Eq. (14) is expected to hold. For $f \gg \kappa q_{\max}^2$, the Marko-Siggia (thermal) limit for large f will prevail.

An alternative way to obtain the force-extension relationship is by taking the derivative of the disorder-averaged free energy given in Eq. (7) with respect to the stretching force: $\partial_f \bar{G}_c = [\langle x(L) \rangle - L]/L$. As expected, both ways yield exactly the same result.

In Ref. [17], it is shown that the effect of annealed disorder in the spontaneous curvature amounts to the replacement of the original bending rigidity κ by $\kappa_{eff} = \kappa / (1 + \Delta_c \kappa / k_B T)$. This implies that for *weak* disorder, defined by $\Delta_c \ll k_B T / \kappa$, the approximate linear relation holds $\kappa_{eff} \approx \kappa (1 - \Delta_c \kappa / k_B T)$ and we immediately recover the response described by Eq. (14). In this regime, quenched disorder has the same effect as annealed disorder. This is the regime treated in Ref. [13]. The difference between the two types of disorder becomes significant in the case of strong disorder, where $\kappa_{eff} \approx k_B T / \Delta_c$. In the quenched case, the second term in the rhs of Eq. (14) dominates the response. In the annealed case, we would have gotten $-\frac{1}{4} \Delta_c L (f_L/f)^{1/2}$ instead which differs by a factor of 2. A more significant qualitative difference between quenched and annealed disorder can be deduced from the form of Eq. (6). Except for the weak regime, the effect of quenched disorder cannot be reduced to a simple renormalization of the bending rigidity.

The force-extension relationship for the random-force system of Eq. (3) can be calculated in a similar fashion, taking into account Eqs. (9) or (10). For strong stretching, $f \gg f_{cr} \gtrsim f_L$, we obtain

$$\frac{\langle x(L) \rangle}{L} - 1 = -\frac{1}{2} \left(\frac{f_{cr}}{f} \right)^{1/2} - \frac{1}{6} \frac{\Delta_g L}{f^2}. \quad (15)$$

We notice that as the stretching force increases, it quickly irons out the bends caused by the random force and the response is dominated by the classical thermal undulations. On the other hand, for given stretching force, bending rigidity, temperature, and disorder strength, the effect of disorder grows linearly with the contour length L and becomes dominant in the thermodynamic limit (f needs to increase accordingly in order to stay within the weakly bending approximation). This is an interesting similarity with the random-force-induced destruction of long-range order in the Abrikosov lattice according to the Larkin model [18]. Comparing Eq. (15) with the result obtained in Ref. [16] for the force-extension relationship of a WLC with sinusoidally varying spontaneous curvature along the polymer contour, we see that the random force effectively acts as spontaneous curvature of that type with amplitude $c_{eff} = (\Delta_g L / 3 \kappa^2)^{1/4}$.

V. TRANSVERSE FLUCTUATIONS

The shape of transverse fluctuations of a stretched filament, $\langle (y(s))^2 \rangle$, is a useful diagnostic tool of its elasticity distinct from its extension in the direction of the pulling force, $\langle x(L) \rangle$ [26]. Using the correlators of Eq. (6), we calculate the width of the transverse fluctuations at the midpoint ($s=L/2$), for $f \gg f_L$, and obtain

$$\left\langle \left(y \left(s = \frac{L}{2} \right) \right)^2 \right\rangle = \frac{Lk_B T}{4} \frac{1}{f} + \frac{\Delta_c \kappa^{3/2}}{4} \frac{1}{f^{3/2}}. \quad (16)$$

For strong disorder, the second term in the rhs of the above equation, which scales as $\sim f^{-3/2}$, can dominate over a range of forces before it is overtaken by the thermal term which scales as $\sim f^{-1}$. In the annealed case the disorder-related term is absent, whereas in the case of weak disorder, $\Delta_c \ll k_B T / \kappa$, it is negligible. We point out that strong quenched disorder in the spontaneous curvature causes a *qualitatively* different behavior in the response of transverse fluctuations which cannot be simply reduced to a renormalization of the persistence length of the undisordered wormlike chain. We see that the claim by Bensimon *et al.* [12] that “a random Kratky-Porod chain with a certain type of disorder is well approximated by a pure chain with an effective elastic constant” is not totally correct. It only applies to the force-elongation curve and cannot be extended to the transverse fluctuations of a strongly disordered WLC.

For the random-force system, the width of the transverse fluctuations at the midpoint ($s=L/2$), for $f \gg f_L$, is given by

$$\left\langle \left[y \left(s = \frac{L}{2} \right) \right]^2 \right\rangle = \frac{Lk_B T}{4} \frac{1}{f} + \frac{\Delta_g L^3}{48} \frac{1}{f^2}. \quad (17)$$

The random-force contribution scales as a higher power of the filament length L and thus is relevant in the long chain limit.

VI. CONCLUSIONS

We studied how the uncorrelated disorder in the spontaneous curvature of a weakly bending WLC affects its response under strong tension. The force-elongation curve for quenched disorder is identical to that of a pure system at a higher temperature. The quenched case is identical to the annealed case in the limit of weak disorder where its effect can be reduced to a decrease in the bending stiffness. This is no longer true as the disorder becomes stronger and our results hold for arbitrary strength. The effect of strong quenched disorder on the force dependence of the width of transverse fluctuations cannot be simply reduced to an effective change in the temperature or the bending stiffness of the pure chain.

We also studied the influence of uncorrelated quenched disorder in the transverse force along the contour of a WLC without spontaneous curvature under tension. In this case, the force-elongation curve is identical to that of a pure WLC with sinusoidal spontaneous curvature. We also find that the effect of the random force increases with the length of the chain. A strong random force may qualitatively alter the force dependence of the transverse fluctuations over a range of pulling forces.

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