Notes

Stiff Chains and Filaments under Tension

Theo Odijk

Faculty of Chemical Engineering and Materials Science, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands

Received April 4, 1995
Revised Manuscript Received July 11, 1995

There is an interesting class of problems in the physics of polymeric materials which one may group under the heading "semiclassical elasticity". Herein, the question is raised how the deformational behavior of the material changes from entropy-dominated to elasticity-dominated as one increases the level of stress exerted on it. Chain fluctuations and undulations are gradually frozen out during this process. Thus, the connotation "semiclassical" applies to an evaluation of the partition function in the limit of weak fluctuations, which may remain influential nonetheless. A simple example of this effect is the elongation of stiff microfilaments under tensions that are of practical interest. Both the fluctuations and material extension in this problem were already addressed qualitatively by Oosawa[1] two decades ago, but a straightforward quantitative analysis is apparently lacking.

Let us suppose it is possible to associate a center curve with the macromolecule or filament in a particular configuration. The center curve is described by the radius vector $\vec{r}(s) = (x(s), y(s), z(s))$, where s is the contour distance from one end. The contour length L is a function of the tension $\vec{f}$ exerted at both ends of the chain (Figure 1). The contour length is L_0 in the state without external stress ($\vec{f} = 0$), referred to here and below by index 0.

The unstressed reference configuration without thermal undulations is assumed to be a straight line. A fairly general, effective Hamiltonian may be written as the sum of three terms

$$\mathcal{H} = \mathcal{H}_b + \mathcal{H}_e + \mathcal{H}_t \tag{1}$$

The bending energy[2] valid for an extendible wormlike chain may be approximated by

$$\mathcal{H}_b = \frac{1}{2}k_B T \int_0^L P(L,s)\left(\frac{\partial^2 \vec{r}}{\partial s^2}\right)^2 ds \tag{2}$$

where k_B is Boltzmann's constant, T is the temperature, and $P(L,s)$ is the persistence length, which will generally depend on the material elongation and hence implicitly on the tension. At the same level of approximation, we have for the energy of material elongation

$$\mathcal{H}_e = \frac{1}{2}\int_0^L K(s,L)\left(\frac{s}{s_0(s)} - 1\right)^2 ds \tag{3}$$

where $K(L,s)$ is an elastic modulus and s/s_0 signifies an extension ratio at s (presumably, there is a one-to-one correspondence between s_0 and s). In principle, both P and K depend on s because both the bending and extension are nonuniform. According to eqs 2 and 3, the filament behaves locally like an elastic medium. The tensile energy follows from considering the displacement of the two ends

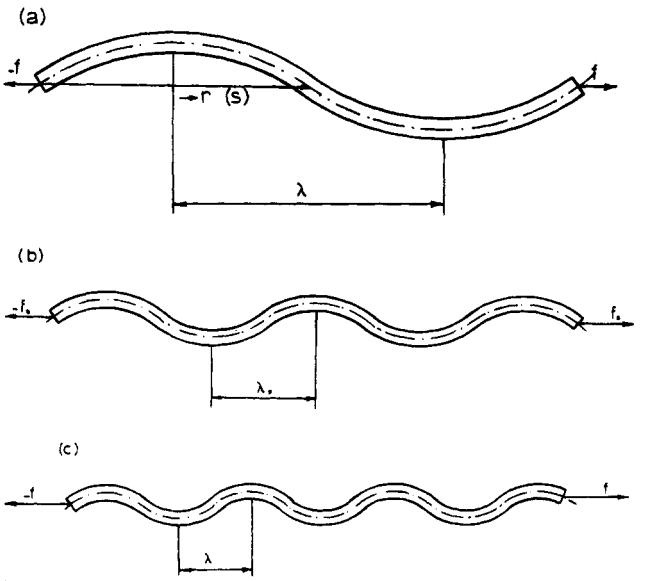

Figure 1. Stiff chain under a gradually increasing tension: (a) undulation-dominated elongation; (b) at the crossover; (c) elasticity-dominated regime.

$$\mathcal{H}_t = -\vec{f}\cdot(\vec{r}(L) - \vec{r}(0)) \tag{4}$$

The statistical physics of a filament or chain defined by $\mathcal{H}$ is obviously complicated but one limit is readily soluble.

I consider the case of small elongations and weak undulations ($\Delta L \equiv L - L_0 \ll L_0$; $dx/ds \simeq \theta_x \ll 1$ and $dy/ds \simeq \theta_y \ll 1$ if $\vec{f} = f\vec{e}_z$ is in the z direction and $\vec{\theta} = (\theta_x(s), \theta_y(s))$ is the angle between the tangential vector $d\vec{r}/ds$ and $\vec{e}_z$. All quantities in eqs 1−4 are now expanded systematically in ΔL and the small angle $\vec{\theta}(s)$ and only the leading terms are retained. The resulting harmonic approximation reads

$$\mathcal{H}_h[\vec{\theta}(s);\Delta L] = \frac{1}{2}k_B T P_0 \int_0^{L_0}\left(\frac{d\vec{\theta}}{ds}\right)^2 ds + \frac{1}{2}f\int_0^{L_0}\vec{\theta}^2\, ds - f\Delta L + \frac{1}{2}K_0 L_0^{-1}\Delta L^2 \tag{5}$$

At this stage the canonical variables $\vec{\theta}(s)$ and ΔL are completely separable and the statistics becomes a matter of quadrature. For instance, a quantity of experimental relevance is the elongation

$$R_z \equiv \vec{e}_z\cdot(\vec{r}(L) - \vec{r}(0)) \simeq L_0 + \langle\Delta L\rangle_h - \frac{1}{2}L_0\langle\theta^2\rangle_h \tag{6}$$

where $\langle\ \rangle$ denotes canonical averaging and higher order terms are consistently deleted in the harmonic approximation. The first average in eq 6 involves essentially Gaussian integrals since $\Delta L \ll L_0$

0024-9297/95/2228-7016$09.00/0

$$\langle \Delta L \rangle_h = f K_0^{-1} L_0 \tag{7}$$

The second average has been computed in a different context for finite contour lengths (see eq IX.8 of ref 3).

$$\langle \theta^2 \rangle_h = \frac{k_B T}{f L_0}\left[1 + \left(\frac{f L_0^2}{P_0 k_B T}\right)^{1/2} \coth\left(\frac{f L_0^2}{P_0 k_B T}\right)^{1/2}\right] \tag{8}$$

The general form of this expression was first derived by Fixman and Kovac[4] although with different numerical coefficients because they employed an approximation, Gaussian in the extension vector, which was forced to mimic a wormlike chain. Their formula also describes the approach to the fully flexible limit. A convenient closed expression valid for sufficiently long contour lengths has been presented recently.[5]

Let us now focus on chains longer than the deflection length[3,9] $\lambda = P_0\langle\theta^2\rangle_h$ so that eqs 6 and 8 reduce to

$$\langle \theta^2 \rangle_h = \left(\frac{k_B T}{f P_0}\right)^{1/2} \tag{9}$$

$$e \equiv \frac{R_z}{L_0} = 1 - \frac{1}{2}\left(\frac{k_B T}{f P_0}\right)^{1/2} + K_0^{-1} f \tag{10}$$

The extension ratio e is defined with respect to the reference state. Equation 10 at zero material elongation (i.e., with $K_0 = \infty$) has been discussed before[6,7] and expresses the manner in which undulations are frozen out as we increase the tension. Here, the curve of e against $\ln f$ has a point of inflection given by

$$f_* = \frac{1}{4}\left(\frac{k_B T K_0^2}{P_0}\right)^{1/3} \tag{11}$$

It effectively demarcates the regime dominated by entropy ($f < f_*$) from that dominated by energy ($f > f_*$), loosely speaking (in practice, the entropy and energy terms are not pure).

In general, there need not be a simple relation between the empirical constants K_0 and P_0. We gain more insight into the magnitude and nature of the crossover given by eq 11 by supposing the macromolecules behaves like a cylindrical rod of homogeneous elasticity. Sometimes this may be a realistic model; often it must be regarded as a convenient idealization. The quantities K_0 and P_0 are now related[2,8] through Young's modulus E and the rod diameter D_0.

$$P_0 = \frac{\pi D_0^4 E}{64 k_B T} \tag{12}$$

$$K_0 = \frac{\pi}{4} D_0^2 E = 16 k_B T P_0 D_0^{-2} \tag{13}$$

These equations yield a numerically transparent formula for the tension at the crossover

$$f_* = \frac{k_B T}{D_0}\left(\frac{4P_0}{D_0}\right)^{1/3} = k_B T\left(\frac{\pi E}{16 k_B T}\right)^{1/3} \tag{14}$$

It is surprising, perhaps, that f_* is independent of the diameter. In addition, we have the following relations valid at the point of inflection

$$\langle \theta^2 \rangle_* = 2^{-1/3}\left(\frac{D_0}{P_0}\right)^{2/3} \tag{15}$$

$$\frac{\Delta L_*}{L_0} = \frac{1}{16}\left(\frac{2D_0}{P_0}\right)^{2/3} \tag{16}$$

Hence, for stiff filaments these ratios are indeed much smaller than unity as is required for the applicability of the harmonic approximation. Equation 15 yields the deflection length[3,6,7,9] at the crossover

$$\lambda_* \equiv P_0\langle\theta^2\rangle_* = 2^{-1/3} D_0^{2/3} P_0^{1/3} = D_0^2\left(\frac{\pi E}{128 k_B T}\right)^{1/3} \tag{17}$$

Accordingly, at $f = f_*$ the transverse distance the filament wanders at most[9] is then D_0 so, for higher tensions ($f > f_*$), it looks progressively more like a straight, smooth rod on the scale of D_0 (Figure 1).

If the elastic rod model is indeed realistic for biofilaments, Young's modulus E would range from 10 to 10^2 $k_B T\,\mathrm{nm}^{-3}$ judging from the dimensions and persistence lengths of DNA,[10] Schizophyllan,[11] fd virus,[12-14] myosin,[15] and F-actin.[16-18] Thus, the tension f_* lies in a narrow range of 1–3 $k_B T\ \mathrm{nm}^{-1}$ and for practical purposes may be regarded a fairly constant and universal quantity in that case. The associated stresses are at MPa levels or less which are on the order of those pertinent to the deformation of many biomaterials.[19] The effect of undulations is particularly evident for filaments longer than the deflection length λ_* though the latter is surprisingly short: from eq 17 its numerical value in nm is basically D_0^2 when D_0 is expressed in nm. Therefore, the simple calculations presented here may bear on a variety of materials from microfibrils within fibers[20-23] to collagen fibrils in structural tissues.[24-26] Finally, measurements of the tensile elongation of a single DNA molecule have been carried out by Smith et al.[27] Their data have been reanalyzed in ref 5 and start to show deviations from purely entropic behavior at a tension of about 10 pN (it is difficult to discern a point of inflection in their $e-\ln f$ curve since there are few data at higher tensions). This onset does agree with eq 14 but more experiments are needed to investigate whether an elastic rod model is indeed appropriate for a complex polymer like DNA in this range of tensions. Recent work[28] shows that, ultimately, the DNA helix may well be disrupted at tensions as high as 50 pN. Yet another effect has been suggested on theoretical grounds by Marko and Siggia,[29] the scale dependence of electrostatics with increasing tension. All in all, with so many regimes, unequivocal determination of the persistence length of DNA from its extensional behavior is nontrivial.

References and Notes

(1) Oosawa, F.; Fujime, S.; Ishiwata, S.; Mihashi, K. *Cold Spring Harbor Lab.* **1973**, *37*, 277.
(2) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(3) Odijk, T. *Macromolecules* **1986**, *19*, 2313.
(4) Fixman, M.; Kovac, J. *J. Chem. Phys.* **1973**, *58*, 1564.
(5) Bustamente, C.; Marko, J. F.; Siggia, E. D.; Smith, S. *Science* **1994**, *265*, 1599.
(6) Williams, D. R. M.; Halperin, A. *Macromolecules* **1993**, *26*, 4208.
(7) Odijk, T. *Macromolecules* **1993**, *26*, 6897.
(8) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*; Pergamon: Oxford, 1986.

(9) Odijk, T. *Macromolecules* **1983**, *16*, 1340.
(10) Taylor, W. H.; Hagerman, P. J. *J. Mol. Biol.* **1990**, *212*, 363.
(11) Yanaki, T.; Norisuye, T.; Fujita, H. *Macromolecules* **1980**, *13*, 1462.
(12) Maeda, T.; Fujime, S. *Macromolecules* **1985**, *18*, 2430.
(13) Beck, K.; Duenki, R. M. J. *Struct. Biol.* **1990**, *105*, 22.
(14) Song, L.; Kim, U. S.; Wilcoxon, J.; Schurr, J. M. *Biopolymers* **1991**, *31*, 547.
(15) Mochizuki-Oda, N.; Fujime, S. *Biopolymers* **1988**, *27*, 1389.
(16) Yanagida, T.; Nakase, T.; Nishiyama, K.; Oosawa, F. *Nature* **1984**, *307*, 58.
(17) Burlacu, S.; Janmey, P. A.; Borejdo, J. *Am. J. Physiol.* **1992**, *262*, C569.
(18) Gittes, F.; Mickey, B.; Nettleton, J.; Howard, J. *J. Cell Biol.* **1993**, *120*, 923.
(19) Vincent, J. *Structural Biomaterials*; Princeton University Press: Princeton, NJ, 1990.
(20) Allen, S. R.; Farris, R. J.; Thomas, E. L. *J. Mater. Sci.* **1985**, *20*, 4583.
(21) Cohen, Y.; Thomas, E. L. *Macromolecules* **1988**, *21*, 433.
(22) Sawyer, L. C.; Jaffe, M. *J. Mater. Sci.* **1986**, *21*, 1897.
(23) Sawyer, L. C.; Chen, R. T.; Jamieson, M. G.; Musselman, I. H.; Russell, P. E. *J. Mater. Sci. Lett.* **1992**, *11*, 69.
(24) Vaughan, L.; Mendler, M.; Huber, S.; Bruckner, P.; Winterhalter, K. H.; Irwin, M. I.; Mayne, R. *J. Cell. Biol.* **1988**, *106*, 991.
(25) Kadler, K. E.; Hulmes, D. J. S.; Hojima, Y.; Prockop, D. J. *Ann. N.Y. Acad. Sci.* **1990**, *580*, 214.
(26) Birk, D. E.; Zycband, E. I.; Winkelmann, D. A.; Trelstad, R. L. *Ann. N.Y. Acad. Sci.* **1990**, *580*, 176.
(27) Smith, S. B.; Finzi, L.; Bustamente, C. *Science* **1992**, *258*, 1122.
(28) Smith, S. B.; Cui, Y.; Hansrath, A. C.; Bustamente, C. *Biophys. J.* **1995**, *68*, A250.
(29) Marko, J. F.; Siggia, E. D., preprint, submitted to *Macromolecules*.

MA950465N