Force-Extension Relation and Plateau Modulus for Wormlike Chains

Klaus Kroy and Erwin Frey
Institut für Theoretische Physik, Technische Universität München,
James-Franck-Straße, 85747 Garching, Germany
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We derive the linear force-extension relation for a wormlike chain of arbitrary stiffness including entropy elasticity, bending and thermodynamic buckling. From this we infer the plateau modulus \( G^0 \) of an isotropic entangled solution of wormlike chains. The entanglement length \( L_e \) is expressed in terms of the characteristic network parameters for three different scaling regimes in the entangled phase. The entanglement transition and the concentration dependence of \( G^0 \) are analyzed. Finally we compare our findings with experimental data.

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Recently there has been increasing interest in biological material research \([1]\). The physical properties of colloids, liquid crystals and macromolecular networks are of prime importance for the structure and function of biological entities such as cells and muscles. On the other hand biology provides physicists with some of the most pertinent model systems to test their theories of soft matter \([2]\). Among these systems we will concentrate on macromolecular networks here. These networks may be assemblies of relatively flexible (DNA), semiflexible (actin) or rigid (microtubuli) molecules or complex compound systems as in the case of the cytoskeleton of erythrocyte plasma membranes or in the glass body of the eye \([3]\). Especially the static and dynamic rheological properties of actin networks are crucial for an understanding of the mechanical stabilization and the motility of cells.

Solutions of flexible polymers at high concentration are known to exhibit spectacular features in both their mechanical response and molecular relaxation \([4]\), which are commonly attributed to the topological constraints due to the uncrossability of the polymers (entanglement). For time scales shorter than a characteristic time \( \tau \) the response of a solution of high molecular weight polymers to a periodic perturbation is elastic over an extended frequency interval ("rubber plateau") and resembles that of a permanently crosslinked network or gel. It is commonly agreed that polymeric liquids form a temporary network, where entanglements play a similar role as permanent crosslinks in gels. There have been several attempts to derive this successful phenomenological concept from other characteristic parameters of a polymer solution and thus gain some understanding of the underlying microscopic mechanisms \([4]\). Over the last few years experiments with actin \([5,6]\) revealed that the above qualitative picture also holds for semiflexible polymers. However, the theoretical understanding of entangled solutions of semiflexible polymers is much less developed than in the flexible case, and experimental data are often interpreted within the theoretical framework established for flexible coils or rigid rods respectively \([7,8]\).

In this letter we develop some basic concepts for a general theory of rheology of isotropic entangled solutions of wormlike chains. The wormlike chain \([9]\) is the minimal model of an ideal (i.e. non self-avoiding) polymer of arbitrary stiffness. In contrast to the fractal Gaussian chain model \([10]\), which can serve only as an effective large scale model for rather flexible polymers, the wormlike chain model also faithfully reproduces the intrinsic stiffness of real polymers. The polymer is represented as a differentiable space curve \( R_s \) with its statistical properties determined by the effective free energy

\[
H (\{ R_s \}) = \frac{\kappa}{2} \int_0^L ds \left( \frac{\partial^2 R_s}{\partial s^2} \right)^2.
\]

A central feature of this model is the inextensibility of the chain leading to the rigid constraint \( |\partial R_s/\partial s| = 1 \), which additionally has to be imposed on the contour. Due to the mathematical complications resulting from this constraint only few of the statistical properties of the wormlike chain can be extracted analytically, the most prominent being the mean square end-to-end distance \( \langle R_s^2 \rangle = L^2 f_D (L/L_p) \), with the Debye function \( f_D(x) := 2(x - 1 + e^{-x})/x^2 \). (The persistence length \( L_p \) is related to the bending modulus \( \kappa \) by \( \kappa = L_p k_B T \).) For large \( L/L_p \) this reduces to the power law \( \langle R_s^2 \rangle = 2 L_p L \) characteristic of a random walk of step length \( 2 L_p \). Note that the model does not reproduce the swelling of real flexible coils, since the self-avoidance of the chain is neglected in the above effective free energy, Eq. \([4]\). Therefore, the model is restricted to solutions with mesh size \( \xi_m \) not much larger than the persistence length \( L_p \) of the polymers, in which case self-avoidance effects can safely be neglected.

As a first step towards an understanding of the macroscopic viscoelastic properties of an entangled network of wormlike chains one has to understand the elastic properties of a single wormlike chain. The linear force-extension relation of a wormlike chain is obtained by the following argument. Consider a wormlike chain with one end clamped at fixed orientation at the origin. Apply a weak

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force $f n$ (directed along the unit vector $n$) to the other end $[13]$. The configurational distribution function is then modified by a Boltzmann factor $\exp(f n R_L/k_B T)$. The extension $\delta R_L := n ((R_L) f - (R_L))$ in the direction of the applied force to first order $f$ is given by the linear extension coefficient $\tilde{f}^{-1}_{\theta_0} := \partial \delta R_L / \partial f |_{f=0}$,

$$\tilde{f}^{-1}_{\theta_0} = \int ds \int ds' \langle \cos \theta_s \cos \theta_{s'} \rangle - \left( \int ds \langle \cos \theta_s \rangle \right)^2. \tag{2}$$

By $\theta_s$ we denote the tilt angles of the tangents of the polymer contour with respect to $n$. The thermal average is to be taken under the constraint that the angle $\theta_0$ at the clamped end is kept fixed. Standard methods $[11]$ yield for $\tilde{f}^{-1}_{\theta_0}$ the dashed curves in Fig. 1. In general, Eq. (3) predicts a polymer of contour length $L$ to appear more floppy if $L_p \approx L$ than in the high temperature limit ($L_p \to 0$) and the low temperature limit ($L_p \to \infty$), when it contracts to a little ball or becomes a rigid rod respectively. In the flexible limit, where the chain becomes an isotropic random coil, all curves fall together and reproduce entropy elasticity. But for stiff chains, as a consequence of the chain anisotropy, the force-extension relation depends strongly on the value of $\theta_0$. Obviously, $\theta_0 = 0$ is an exceptional case. Whereas for all other angles $\theta_0$ the ultimate asymptotic form of $\tilde{f}_{\theta_0}$ in the stiff limit is $\kappa/L_3$, at $\theta_0 = 0$ the force coefficient becomes $\tilde{f}_0 \approx \kappa^2/2 k_B T L^4$; i.e. it is second order in the bending modulus and diverges at low temperatures $T$. The latter result was previously obtained in Ref. $[13]$. Note that $\theta_0$ is the angle between the applied force and the average orientation of $R_L$, i.e. for $\theta_0 = 0$ the force is parallel to $R_L$ on average. Especially for $T = 0$ the force is pulling or pressing on a rigid rod along its axis. In this limit the above expansion of the Boltzmann factor breaks down and we encounter the so called Euler buckling instability, i.e., the force-extension relation becomes highly nonlinear and the force coefficient in linear response does not exist. This situation is well known for foams and other cellular materials $[4]$. If we require $f R_L \ll k_B T$, the buckling instability is evaded by thermal undulations, and we find a linear contribution to the force-extension relation (‘thermodynamic buckling’). But with decreasing temperature the volume fraction $k_B T L / \kappa$ (stored thermal energy over bending energy) occupied by the thermal undulations vanishes, and ultimately there remain no more undulations to be bent or pulled out, hence the divergence of $\tilde{f}_0$ with $T^{-1}$. We take as the force coefficient $\tilde{f}$ of a ‘general strand’ of length $L$ in a random network the average of $\tilde{f}^{-1}_{\theta_0}$ over all orientations $\theta_0$ $[13]$:

$$\tilde{f}^{-1} = L^2 f_{ext}(L/L_p)/k_B T, \tag{3}$$

with $f_{ext}(x) := (2x - 3 + 4e^{-x} - e^{-2x})/3x^2$ (the extension function). This result is also shown in Fig. 1. In the stiff limit ($L \ll L_p$) it reduces to $\tilde{f} \approx \kappa/L_3$. Now, to relate the force-extension relation of the general strand to the observed elastic modulus of a polymer network in the rubber plateau regime we proceed in close analogy to solid state physics. In the harmonic approximation the elasticity tensor $E$ of a monatomic Bravais lattice is written as $E_{ijkl} = -\sum_{(R)} R_i D_{jl}(R) R_k/2V$, with $V$ being the volume of the primitive cell, $R$ the lattice vectors and $D$ the matrix of second derivatives of the interaction potential with respect to lattice displacements. For an isotropic entangled polymer solution, we take the analogue of the primitive cell to be an entanglement volume $V_e$ and the analogue of the primitive vectors to be the average distance $\xi_e$ between adjacent entanglements (in the embedding space). This scaling argument suggests that the storage modulus in the plateau regime should (up to a constant factor depending on the strain geometry) be given by $G^0 \approx c_e \tilde{f} e_k \tilde{c}_e$. Here $f_e$ is the force coefficient of polymer sections of length $L_e$ between adjacent entanglements and $c_e \approx V_s^{-1}$ their concentration. (As far as self-avoidance effects can be neglected, $L_e$ and $\xi_e$ are related by the Debye function.) The situation may be visualized by external forces acting on contour elements distributed with an average spacing $L_e$ along the polymer. Inserting $\tilde{f}$ from Eq. (3) with $L_e$ substituted for $L$ into the formula for $G^0$ we finally arrive at the following explicit expression for the plateau modulus of an entangled solution of wormlike chains,

$$G^0 \approx c_e k_B T \frac{f_{ext}(L_e/L_p)}{f_{ext}(L_e/L_p)} \sim \begin{cases} c_e k_B T & (L_e \gg L_p) \\ c_e \frac{1}{V_e} & (L_e \ll L_p). \end{cases} \tag{4}$$

The entanglement length $L_e$ is obviously the crucial quantity in Eq. (4). In the literature several scaling ideas $[3]$ have been reported on how $L_e$ and $\xi_e$ may be derived from the known static properties of a flexible polymer network. Note however that Eq. (4) holds independently of such considerations. For a homogeneously crosslinked
gel of semiflexible or rod-like polymers \( \xi_e \) can essentially be identified with the mesh size \( \xi_m \) of the network. In this case Eq. (4) predicts \( \xi^0 \propto \kappa c^2 \) in the stiff limit. We conjecture that for a solution of wormlike chains of arbitrary stiffness one has to distinguish three different regimes. We will treat the limiting cases of scale invariant chain structure – i.e. a virtually Gaussian or straight conformation respectively – in a very similar manner. The breaking of scale invariance due to Eq. (4) gives rise to an intermediate regime for chains with \( L \approx L_p \), which will be discussed subsequently.

For a weakly bending contour we have from Eq. (4) the scaling relation \( R^2_L \propto 2L^3/3L_p^2 \) for the transverse amplitudes \( R^2_L \) of the largest bending undulations. If these amplitudes are smaller than the mesh size \( \xi_m \) of the surrounding polymer network, i.e. \( \xi_m^2 > 2L^3/3L_p^2 \), then the bending undulations are not substantially perturbed and are supposed to be rather irrelevant to the question of entanglement. In this case we should thus be allowed to represent the polymers as straight (but not rigid) “rods” in our derivation of \( L_e \). In the opposite extreme \( (L, \xi_m \gg L_p) \) of a strongly coiled polymer conformation the polymer may be represented by a fractal curve (or a freely jointed chain of “blobs”, if screened self-avoidance is to be included). We feel that the flexible case has been described successfully earlier [15] and will adapt this approach to straight rods now. It is based on the crucial observation that polymer ends are not contributing efficiently to long-lived entanglements. Namely, if entanglements would depend on dangling ends, they could not be long-lived as compared to unperturbed, free fluctuations of the polymer and hence could not give rise to a rubber plateau. To be specific, we assume that an entanglement requires a sufficient number of non-end neighboring polymer segments that on average restrict the lateral degrees of freedom of a test chain. Consider a sphere of radius \( \xi_e \) around such a mean entanglement point. Then for a given monomer concentration \( c \) and volume fraction \( cv \) the excluded volume in this “primitive cell of entanglement” of volume \( V_e = 4\pi(\xi_e/2)^3/3 \) is given by \( cvV_e \). In order to achieve an entanglement one requires that a certain amount of polymer material, \( c\pi (a/2)^2 L_e \), is contained in the test volume. Here \( a \) denotes the lateral diameter of the polymer. The quantity \( \mathcal{C} \) is a geometry factor which measures the amount of polymer material in the test volume, if \( K \) polymers cross the sphere around the test chain [14]. We determine \( L_e \) by equating the excluded volume (reduced by the contribution coming from free ends) with the volume of polymer material needed for an entanglement

\[
(cv \left( 1 - \frac{L_e}{L} \right) = \frac{3a^2L_eC}{2\xi_e^3}.
\]

The implicit equation Eq. (5) can be solved analytically in the random coil limit [16] and for a straight conformation. For the latter we find

\[
L_e = \frac{L}{3} \left\{ 1 - 2 \sin \left[ \frac{1}{3} \arcsin \left( 1 - \frac{27L^2c^2}{4L^2} \right) \right] \right\}, \quad (6)
\]

where \( L_e^\infty := a\sqrt{3c/2cv} \approx \sqrt{c\xi_m} \) is the entanglement length in the limit of infinitely long molecules. Eq. (4) describes an entanglement transition of the polymer solution characterized by a cusp singularity of the entanglement length \( L_e \) as a function of the polymer length \( L \) or the volume fraction \( cv \). The phase boundary between the entangled and the disentangled regime is given by either of the two equations \( c^*(L) = 27cC(L)/4, \quad L^*(c) = 3\sqrt{3}L^\infty(c)/2 \), where \( \bar{c} \) denotes the geometrical overlap concentration \( \bar{cv} = 3a^2/2L^2 \). The value of the entanglement length and the contour length at the cusp singularity are related by \( L_e^* = 2L^*/3 \). The above results have some important consequences on the rheological properties of semiflexible polymer solutions. Upon taking the experimental value for the geometric constant \( C = 9.1 \) [16] of flexible polymers to be a universal quantity (also valid in the rod-limit) one estimates that the critical polymer length for the solution to show entanglement has to be about eight times the mesh size. Accordingly, the critical concentration \( c^* \) is predicted to be almost two orders of magnitude larger than the overlap concentration \( \bar{c}, \quad c^*/\bar{c} = 27C/4 \). In the intermediate concentration regime, \( c^* > c > \bar{c} \), there is already a significant overlap of the semiflexible polymers but no long-lived entanglements leading to a rubber plateau regime. In this disentangled phase the magnitude of the storage modulus is supposed to show a linear concentration dependence.

Finally we comment shortly on the intermediate case of a network of wormlike chains with a mesh size \( \xi_m \) smaller than the persistence length \( L_p \) and the amplitudes of the largest bending undulations \( R^2_L \). To distinguish it from the discussed above, which could be called the “rod-like” regime, we will address it as the “snake-like” regime. It is characterized by the property that all bending undulations with wavelength longer than a critical wavelength, the “deflection length” [17] \( \lambda \simeq (3L_p\xi_m^2/2)^{1/3} \), are perturbed by the network. For the snake-like regime we thus identify the entanglement length \( L_e^\infty \) for an infinitely long polymer with \( \lambda \). We expect the qualitative features of the entanglement transition derived above for the rod-like regime to hold also in the snake-like regime. The isotropic entanglement volume \( V_e \equiv \xi^5_e \) in Eq. (4) has now to be replaced by \( V_e \equiv \xi_e R^2_L \). The implicit dependence of \( V_e \) on \( L_p \) again reflects the broken scale invariance in the snake-like regime. We leave the problem of the crossover between the snake-like and the scale invariant cases for further investigation.

Now we turn to the comparison of our results with available experimental data. We suppose that the existence of a disentangled phase above the overlap concentration \( \bar{c} \), as predicted by Eq. (3), is likely to explain some discrepancies of the Doi-Edwards theory [18] for
the rotational diffusion of rigid rods in a semidilute solution with experimental data [20]. The Doi-Edwards theory is based on the assumption that for concentrations larger than the overlap concentration \(c^\ast\) there is a separation of time scales. One anticipates that each step of the rotational diffusion process is determined by the constraint that each rod is confined to remain within an angular range \(\xi_T/L\) during the time it takes a rod to diffuse a distance equal to its length. The tube of radius \(\xi_T \propto 1/cL\) is assumed to impose a long-lived topological restriction on the motion of the rods. However, as we have argued above, long-lived entanglements emerge only at a much higher concentration \(c^\ast = 27\overline{c}/4\). This would explain why the onset of entanglement as defined by a marked decrease in the rotational diffusion coefficient occurs at a concentration \(c_{\text{exp}}\) fully two orders of magnitude above the overlap concentration [20].

As an important practical application of the above ideas we already mentioned actin, a semiflexible macromolecule, which is of major biological interest but is also an almost ideal model system for physicists [21]. It is well suited to test our ideas, because it is characterized by a large ratio \(L_p/a\) (\(\simeq 10^3\)) and thus by a broad semidilute regime, so that the wormlike chain model applies without modification over several orders of magnitude in concentration. The average length of the molecules can be adjusted by adding so called actin binding proteins such as gelsolin or severin. Existing data on actin [8,9,22] give only an incomplete picture of the rather complex situation sketched above but seem to support our results. For short (rod-like) filaments a length dependence of the plateau modulus near the entanglement transition has been observed [7], which is qualitatively well described by Eq. (4) and (3), but is somewhat smeared out (probably as an effect of sample polydispersity). In the entangled phase Eq. (1) together with Eq. (6) predicts a plateau modulus \(G^0 \propto \kappa c^2\) for the rod-like case far from the entanglement transition. Near the transition the concentration dependence is enhanced according to Eq. (6). In the snake-like case as defined above we have \(L_e \simeq (L_p c^2)^{1/3}\) with \(\xi_m \propto c^{-1/2}\) and hence \(G^0 \propto c^{5/3} \kappa^{1/3} (k_BT)^{2/3}\). In experiments with actin the exponent of the observed power law for \(G^0(c)\) ranges from 1.7 to 2.3 in the entangled regime [15,16,22]. As a critical test of our ideas we suggest a comparison of the plateau modulus for actin networks with and without tropomyosin, which is known to cause a considerable stiffening of actin filaments. The rod-like regime and the snake-like regime should be readily discernible due to their markedly different dependence of \(G^0\) on \(c\).

In summary, we have derived the force-extension relation for a wormlike chain and discussed some of its consequences for the viscoelastic properties of entangled solutions and gels of semiflexible polymers. Especially, we analyzed the entanglement transition and predicted various exponents for the dependence of the plateau modulus \(G^0\) on concentration and bending rigidity.

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polymer crossing the test volume will in general not go through the center of the sphere. Elementary geometrical considerations suggest that in this case the coordination number is $K = 16(C - 1)/3\pi$. Hence for a given value of $C$ the number of nearest neighbors involved in an entanglement is larger for semiflexible polymers as compared to random coils. This is in accord with ones intuition that flexible coils, resembling interpenetrating fuzzy balls, are more efficient in mutual entanglement than semiflexible polymers, which are rod-like on short scales.

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