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Stress strain relations in semiflexible networks

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ABSTRACT

We explore theoretically the zero frequency shear modulus of a polymer network constructed from semiflexible polymers and find that the mechanical properties can be varied remarkably by small changes in the length of the constituent polymers or cross-linker density. This sensitive dependence of rheology upon network microstructure is due to the presence of a cross-over from a regime of affine deformation under uniformly applied stress to one of spatially heterogeneous, nonaffine deformation signally the breakdown of continuum elasticity of significant mesoscopic length scales. This cross-over from affine to nonaffine deformation may play an important role in the understanding of the rheology of the cytoskeleton. Moreover, the presence of this cross-over suggests a new mechanism for the construction of highly adaptive gels based on a biomemetic design motif.

INTRODUCTION

Semiflexible gels may be defined as cross-linked polymer networks in which the mean distance between cross links is less than the thermal persistence length of the constituent polymers. Thus, the microstructure of the solid is better described as an interwoven mesh of flexible rods rather than the canonical picture of a network of entropic springs used to describe gels constructed from flexible polymer chains. In this note we focus our discussion solely on the rheological properties of such networks. Nevertheless, to explain our interest (and that of numerous other groups) in these materials we point out that such semiflexible gels are in fact highly ubiquitous in nature as they form the cytoskeleton of all eukaryotic cells [1]. This intracellular structure constructed primarily of cross-linked semiflexible protein filaments is source of cellular mechanical integrity, motility, and is implicated in the ability of certain cells to sense and response to their external stress environment.

In this note we summarize recent results [2,3] suggesting that semiflexible networks are remarkably adaptable materials in the sense that their rheological properties can be dramatically modified via modest chemical changes. This dramatic rheological change is due to breakdown of continuum elasticity on mesoscopic length scales in the material. Under uniformly applied shear stress the statistically homogeneous network can have a highly spatially inhomogeneous strain field over length scales much larger than the mesh size of the network. In particular we show that these semiflexible networks admit a new length scale λ that depends on both the mean spacing between cross-links the thermal persistence length of the constituent filaments. The zero-frequency elastic properties of semiflexible gels depend very sensitively on the dimensionless ratio of the filament length to this new length scale: L/λ.

The ratio L/λ can be thought of as a novel source of the rheological control of adaptive, biomemtic gels based on the design motif perfected in the cytoskeleton. The sensitive dependence of the zero frequency (and low-frequency) rheological properties on filament length emphasizes unusual form of the deformation field in the network. For flexible polymers the zero frequency shear modulus of a gel or the plateau modulus of a polymer solution is independent of the polymerization index and depends only on the mesh size. The underlying cause of the independence of the network's rheological properties on the length of the polymers is that each entanglement length of the polymer chain is an independent dynamical agent in flexible polymers. In semiflexible polymer networks, however, the long thermal persistence length of the chains enforces new long-range mechanical interactions between distant entanglement lengths in the network that happen to part of the same polymer. These long-range interactions extend over the length of the individual polymers so that their length L plays a new role in the rheology of such materials.

The Deformation Field

To explore the mechanical/rheological properties of semiflexible networks we constructed a two-dimensional numerical model of the network. Filaments, which are taken to be straight line segments, are deposited in the shear cell with random orientations and random positions of their center of mass. Whenever two filaments cross, they are permanently linked by a cross-linker that provides arbitrary constraint forces but no constraint torques; filaments are free to rotation at each cross-link. Further angle constraints at each cross-link do not substantially change our results. The structure of the network is represented by the complete set of the coordinates of the cross-links and of the midpoints along each polymer between cross-links. These latter points are included in order to account for first bending mode between any two cross links.

The network thus constructed is stress-field and at its energy minimum. Relative motion of the cross-links and midpoints incurs an energy cost associated with the stretching of the intervening filament of length l_0 by an amount δl according to

$$\delta H_{\text{stretch}} = \frac{\mu}{2}\left(\frac{\delta l}{l_0}\right)^2 l_0, \qquad (1.1)$$

where μ is the extensional modulus of an individual filament. Similarly, a nonzero angle $\delta\theta$ between consecutive chain tangents contributes

$$\delta H_{\text{bend}} = \frac{\kappa}{2}\left(\frac{\delta\theta}{l}\right)^2 l \qquad (1.2)$$

to the energy where l is the mean of the consecutive filament lengths associated with the aforementioned chain tangents. We have introduced the filament bending modulus κ. The network can then be sheared in the standard Lees-Edwards manner and is then relaxed by moving the positions of the midpoints and crossing points according to a conjugate gradient scheme.

Each network so constructed can be described in terms of three lengths: (i) The mean distance between cross-links, l_c, which in two dimensions fully characterizes the structure of the random network, and (ii) the filament length L for the monodisperse rod network, and (iii) a bending length $l_b = (\kappa/\mu)^{1/2}$, which characterizes the elastic properties of the individual rods. Now μ sets the only energy scale in the problem and we report all moduli in terms of μ/L. Further details can be found in reference [3].

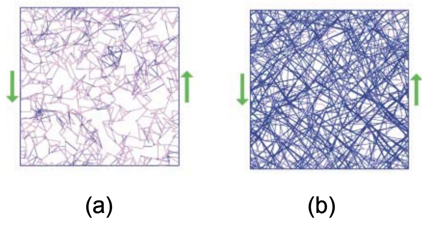
(a) (b)

Figure 1: Sheared semiflexible networks. The lines draw at the undeformed positions of the filaments has thickness proportional to the total elastic energy stored under shear (shown by the green arrows). The color coding reflects the partitioning of that energy into bending (pink) or stretching (blue) deformations of the filament. In (a $L/l_c=9$, while in (b) $L/l_c=47$.

We calculate the elastic modulus of the system from the elastic energy storage at this new minimum. Examples of sheared networks are shown in figure 1. In that figure one observes qualitatively the affine to nonaffine cross-over. In figure 1(a) on the left, the mean number of cross-links along a filament is seven - a density above the rigidity percolation transition in the network [4] but well in the nonaffine regime. Here the network deforms in a highly heterogeneous manner and the elastic energy storage is almost entirely in the bending modes of a few filaments. If one were to increase the mean number of cross-links per filament to *e.g.* 46, the network is now deep into the affine regime where the deformation field is spatially uniform and the elastic energy is stored entirely in the stretching modes of the filaments. The nonaffinely deforming network must have a smaller modulus than the networks in the affine regime. One can imagine imposing an artificial set of constraints on the nonaffine network to enforce affine deformation. Removing those additional constraints the network can only further relax the stored elastic energy hence the moduli of the nonaffine gel will be smaller than in an affine one. To examine this issue more quantitatively we plot in the upper panel of figure 2 the numerically determined shear modulus for a variety of networks having differing filament elastic properties (characterized by L/l_b) and network densities (characterized by L/l_c). We find that these numerical data can be collapsed onto a single master curve provided we scale the observed modulus by prediction of affine network

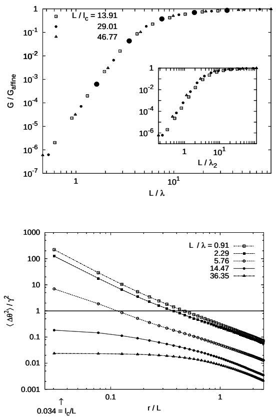

Figure 2 The upper figure shows the dramatic decrease in shear modulus accompanying the cross-over from affine to nonaffine networks. This cross-over is controlled by the L/λ as described in the text. The lower figure directly measures the affinity of the deformation field as a function of length scale in the network. Identical networks are represented by the same symbols to facilitate a comparison.

$$G_{\text{affine}} = \frac{\pi}{16}\frac{\mu}{L}\left(\frac{L}{l_c} + 2\frac{l_c}{L} - 3\right) \tag{1.3}$$

and plot on the abscissa the filament length *L* scaled by the length λ defined by

$$\lambda = l_c \left({l_c}\big/{l_b} \right)^z \tag{1.4}$$

with the exponent z=1/3 to collapse the data.

Geometry and Rheology

It is apparent from the upper panel of figure 2 that there is an extreme sensitivity of the shear modulus upon the dimensionless parameter *L*/λ allowing an $\mathcal{O}(10^6)$ change in modulus for about an order of magnitude change in the control parameter. How are we to understand this unexpected rheological control of the material? The terminology used above suggests that the explanation lies in the geometry (*i.e.* affine vs. nonaffine) of the deformation field in the network. In essence we seek to link collective mechanical or rheological behavior of the network to the geometry of the strain field. To do so we need an independent, purely geometric measure of the deformation field.

To quantify the degree of nonaffinity at a given length scale, consider the infinitesimal change in angle under an imposed shear strain between two network nodes separated by a distance *r*. Denoting this angle by θ and its corresponding affine prediction by θ_{affine}, we arrive at a suitable measure for the deviation from affinity on the length scale r by defining

$$\left\langle \Delta\theta^2(r) \right\rangle = \left\langle \left(\theta - \theta_{\text{affine}}\right)^2 \right\rangle \tag{1.5}$$

where the angled brackets denote averaging over both network points and different network realizations. Clearly at system-spanning length scales we expect that all deformations will be affine as required by the spatially uniform shear. As we further refine our analysis by successively resolving finer and finer network structures, one expects deviations from affinity to grow monotonically. In fact, we see in the lower panel of figure 2 that there are two classes of networks with respect to this measure of nonaffinity. In one the measure of nonaffinity (scaled by the total shear strain γ) plateaus around order 0.1 even down to length scales on the order of the network mesh size; these networks have a shear modulus that is well-described by theories based on mean-field, affine deformation. In nonaffine networks with significantly weaker shear moduli, the purely geometric measure of nonaffinity grows without bound as one resolves deformations on successively finer length scales.

We have shown that semiflexible gels admit a new rheological control parameter that, by changing the geometry of the internal deformation field, can dramatically change the rheological properties of the network through small changes in either the length of the constituent filaments or in the cross-link density. This unprecedented sensitivity of network moduli on gel microstructure suggests the importance of developing a biomemtic semiflexible gel technology.

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