Stiff Polymers, Foams and Fiber Networks

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We study the elasticity of fibrous materials composed of generalized stiff polymers. It is shown that in contrast to cellular foam-like structures affine strain fields are generically unstable. Instead, a subtle interplay between the architecture of the network and the elastic properties of its building blocks leads to intriguing mechanical properties with intermediate asymptotic scaling regimes. We present exhaustive numerical studies based on a finite element method complemented by scaling arguments.

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Cellular and fibrous materials are ubiquitous in nature and in many areas of technology. Examples range from solid or liquid foams over wood and bone to the protein fiber network of cells [1, 2, 3]. On a mesoscopic level these materials are comprised of struts and membranes with anisotropic elastic properties. The systems differ widely in architecture. One finds patterns which are as regular as a honeycomb, as sophisticated as the particular design of a dragonfly’s wing or simply random [4, 5]. The manifold combinations of architectures and elastic properties of the building blocks allows for a rich spectrum of macroscopic elastic responses. For cellular structures (see the foam-like structure in Fig. 1a) macroscopic elasticity can already be understood by considering the response of a single cell [6, 7]. In these systems local stresses acting on an individual cell are the same as those applied on the macroscopic scale. In other words, the local deformation \( \delta \) of a cell with linear dimension \( l_s \) follows the macroscopic strain \( \gamma \) in an affine way such that it scales as \( \delta \propto \gamma l_s \). This affinity of the deformations seems to be a reasonable approximation even for systems with some randomness in the size and the type of their unit cells [8, 9]. Since in affine models there can be no cooperativity between the elastic responses of individual cells, the effect of the assembled structure can simply be predicted by counting the numbers of cells. Fibrous networks, on the other hand, are dramatically different already in their morphology as can be inferred from Fig. 1a. The presence of fibers introduces the additional mesoscopic scale of the fiber length \( l \) and generates a broad distribution of pore sizes that, in contrast to foams, has a non-vanishing weight even for the smallest cells [10]. This difference in architecture crucially affects the mechanical properties. Recently a non-affine regime has been identified [11] and characterized [12, 13, 14, 15] in two-dimensional networks of classical beams (“Mikado model”) commonly used to model the mechanical properties of paper sheets [12, 13, 14, 15]. The non-affinity of the deformation field necessarily implies that in these networks cooperativity effects play an important role.

In this Letter we will address the question of how such non-trivial network geometry generates correlation-induced linear elastic behavior while cellular foam-like structures can generally be described by mean-field like approaches. By systematically tuning the force response properties of the individual elements we will be able to identify a new length-scale below which correlations drive the system away from the state of affine deformations. We will, moreover, describe the mechanism that generates this length and calculate the resulting power law behavior of the elastic modulus by a scaling argument.

The model is defined as follows. \( N \) anisotropic elastic elements, geometrically represented by straight lines of length \( l \), are placed on a plane of area \( A = L^2 \) such that both position and orientation of the elements are uniformly random distributed. The length of the segments, i.e. the distance \( l_s \) between any two neighboring intersections, follows an exponential distribution [12]

\[
P(l_s) = (\langle l_s \rangle)^{-1} e^{-l/l_s},
\]

with a mean value that is given in terms of the density \( \rho = N l / A \) as \( \langle l_s \rangle = \pi / 2 \rho \). At any intersection a permanent crosslink with zero extensibility is generated. This

![FIG. 1: Illustration of the different architecture of (a) cellular and (b) fibrous materials. The foam in (a) is constructed by a Voronoi tessellation from the centers of the fibers in (b).](image-url)
contains the relative translational motion of the two filaments, while leaving the rotational degrees of freedom independent (free hinges). Next to the architecture of the network we have to specify the linear elastic properties of the constituents. Previous studies [11] have considered classical beams of radius $r$ and bending stiffness $\kappa$. Loaded along their axis (“stretching”) such slender rods have a rather high stiffness $k_s = 4\kappa/l_s r^2$, while they are much softer with respect to transverse deformations $k_\perp(l_s) = 3\kappa/l_s^2$ (“bending”). Here, we consider elastic elements where in addition to the mechanical stiffness of classical beams a more general stretching coefficient

$$k_{||}(l_s) = 6 \kappa \frac{l_s^2}{l_p^{1+\alpha}},$$

is introduced. This may result from thermal fluctuations of the filament immersed in a heat bath of solvent molecules. The prefactor is chosen such that $k_{||}$ for $\alpha = 1$ reduces to the longitudinal entropic elasticity of a stiff polymer described by the wormlike chain model grafted at one end [12]. In this case the material length $l_p$ is called the persistence length of the polymer and quantifies the ratio of bending to thermal energy $l_p = \kappa/k_B T$. The phenomenological exponent $\alpha$ allows us to extend our discussion to the broad class of systems for which $k_{||}$ is a monomial (with units energy per area) involving one additional material length $l_p$. Having two longitudinal deformation modes the effective stretching stiffness is equivalent to a serial connection of the “springs” $k_s$ and $k_{||}$. Setting $l_p = cr$, we can write $k_s \propto k_{||}(\alpha = -2)$. The constant $c$ is a material property of the specific polymer and has been chosen as $c = 1.5 \cdot 10^4$, which roughly corresponds to the biopolymer F-actin. The precise value, however, is irrelevant what regards the thermal response $k_{||}$ and only specifies the location of the cross-over to $k_s$. The description of a thermally fluctuating network in terms of force constants $k_{||}$, $k_s$ and $k_\perp$ is in the spirit of a Born-Oppenheimer approximation that neglects the fluctuations of the “slow variables”, the cross-link positions, while assuming the “fast” polymer degrees of freedom to be equilibrated. By minimization of the internal energy with respect to the slow parameters, the modulus for a given macroscopic deformation can be calculated. In practice, we apply a shear strain of $\gamma = 0.01$ and thus determine the shear modulus $G$ using periodic boundary conditions on all four sides of the simulation box. The minimization procedure is performed with the commercially available finite element solver MSC.MARC.

To set up a reference frame, it is instructive to discuss a mean-field approach which assumes that correlations between neighboring segments are absent. As outlined in the introduction this corresponds to a foam-like behavior, where the response is fully described by the properties of an average segment of length $\langle l_s \rangle \propto \rho^{-1}$. Marking the force constants of this segment by an overbar, we can express them in the form (neglecting numerical prefactors)

\[
\bar{k}_s \approx \kappa \rho^3, \quad \bar{k}_\parallel \approx \bar{k}_\perp (\rho l_p)^{\alpha} \quad \text{and} \quad \bar{k}_\perp \approx \bar{k}_\perp (\rho r)^{-2},
\]

The network will thus show a crossover from thermal stretching to bending at $l_p \approx \langle l_s \rangle$ and to mechanical stretching at $r \approx \langle l_s \rangle$. This behavior is indicated by the dashed line in Fig. 2 where it can be compared with the actual results of our numerical analysis. The normalized shear modulus $G \rho^3/\kappa$ is shown as a function of dimensionless persistence length $l_p/l$ for a set of dimensionless densities $\rho l_p$. At large $l_p/l$ (in the right part of the plot) we recover purely mechanical behavior characterized by $G \propto \bar{k}_\parallel$, consistent with the mean-field picture of Eq. (3). Our main interest, however, lies in the regime of small $l_p/l$ (in the left part of the plot), where the persistence length is small enough for thermal fluctuations to become relevant. To analyze the modulus in the thermal regime (where $k_s$ is irrelevant) it will be helpful to use dimensional analysis and write the modulus in terms of the two remaining response coefficients $\bar{k}_\parallel$ and $\bar{k}_\perp$ of an average segment

\[
G(\kappa, l_p, \rho) = \bar{k}_\parallel g(\rho, \bar{k}_\parallel/\bar{k}_\perp).
\]

The first argument of the scaling function $g$, the density $x = \rho l_p$, is of geometrical origin and counts the number of crosslinks per filament. The second argument, $y = \bar{k}_\parallel/\bar{k}_\perp \approx \rho l_p$, relates to the energy balance between stretching and bending of an average segment and marks a crossover at $y \approx 1$ or $l_p \approx \langle l_s \rangle$. From Fig. 2 and the inset of Fig. 3 one infers that for low densities $g = y f(x)$, implying for the modulus $G = \bar{k}_\parallel f(\rho l_p)$. This linear dependence on the “pre-averaged” stretching compliance
can easily show that the size of these residual forces $\delta f$ can be arbitrarily large. The corresponding probability distribution $Q(\delta f)$ shows polynomial (fat) tails

$$Q(\delta f) \propto \delta f^{-4/3} P(l_s), \delta f \to \infty$$

and has a diverging mean value since $P(l_s = 0) \neq 0$. As a consequence there are always residual forces high enough to cause significant bending of the crossing filament. Hence we conclude that an affine deformation field is unstable and that the system can easily lower its energy by redistributing the stresses to relieve shorter segments and remove the tails of the residual force distribution $Q(\delta f)$.

This mechanism can be used to derive an expression for the modulus in the parameter region $y \ll 1$, where the value of the exponent $z = 0.46$ indicates that bending and stretching deformations contribute equally to the elastic energy. We assume that segments up to a critical length $l_c$ – to be determined self-consistently – will fully relax from their affine reference state to give all their energy to the neighboring segment on the crossing filament. The energy of segments with $l_s > l_c$ will then have two contributions. First, a stretching part from the imposed affine strain field (for simplicity, we will set $\alpha = 1$ in what follows)

$$w_s(l_s) \simeq k_\| \delta f^2 \| \simeq \kappa \gamma l_p^2 l_s^3.$$  

Second, a bending part

$$w_b(l_s) \simeq k_\perp \delta f^2 \perp \simeq \kappa \gamma l_p^2 l_s^3,$$

that only arises if the segment under consideration is neighbor to an element on the crossing filament with $l_s' < l_c$ (the prime refers to the neighboring small segment). Adding both contributions and averaging over all segments $l_s > l_c$ and $l_s' < l_c$ we arrive at the expression

$$w \simeq \kappa \gamma^2 \rho (l_p/x_c + x_c),$$

where $x_c := \rho l_c \ll 1$ in the parameter range of interest. Minimizing with respect to $x_c$ gives the required expressions $x_c^\text{min} \simeq (l_p/\rho)^{1/2}$ and $G \simeq \rho^2 w_{\text{min}}/\gamma^2 \simeq \kappa \rho^{7/2} l_p^{1/2}$ corresponding to a value $z = 1/2$ for the exponent that compares well with the measured value $z = 0.46$. Repeating the calculation for general values of $\alpha$ gives $z(\alpha) = \alpha/(1 + \alpha)$. We have verified this result by simulations with an accuracy of about ten per cent [15]. The non-trivial behavior of $G$ observed in Figs. 2 and 3 can thus be explained by a length scale $l_c = (l_s) (l_p/l_s)^{1/2}$ below which the affinity of the deformation field breaks down. The mechanism is illustrated in Fig. 4 where a histogram for the fraction of energy stored in segments of various lengths is shown. Increasing the persistence length, the short segments one after the other lose their energies in favor of additional excitations in longer segments.
mixed regime we found a stretching dominated regime that is characterized by exponents similar to those obtained in the foam-like stretching regime. Microscopically, however, the stress is distributed in a completely different way and is dominated by very few, very long fiber segments. As mentioned above, one particular application of our model is to the macroscopic linear response of stiff polymer networks. The results may therefore be directly relevant for two-dimensional networks of the filamentous biopolymer F-actin, assembled on top of micro-fabricated pillars [19]. In addition, it might shed new light on very recent rheological measurements on cross-linked actin networks [20, 21], which emphasize the single-polymer origin of the measured elastic moduli. Our simulations, on the contrary, highlight the potentially non-trivial effects of inter-polymer correlations on the macroscopic elasticity.

FIG. 4: Fraction of energy stored in the various segment lengths; the curves correspond to different persistence lengths at a density of \( \rho l = 80 \), equivalent to \( \langle l_s \rangle / l \approx 2 \cdot 10^{-2} \).