Chapter 4

Mechanically-controlled criticality in fiber networks


Abstract

Disordered fiber networks are ubiquitous in nature as major structural components of living cells and tissues. The mechanical stability of networks generally depends on the degree of connectivity: networks become stable only when the average number of connections between nodes exceeds the isostatic threshold [123]. Upon increasing the connectivity through this point, such networks undergo a mechanical phase transition from a floppy to a rigid phase. However, even sub-isostatic networks become rigid when subjected to sufficiently large deformations. To study this strain-controlled transition, we perform a combination of computational modeling of fiber networks and experiments on networks of type I collagen fibers, which are crucial for the integrity of biological tissues. We show theoretically that the development of rigidity is characterized by a strain-controlled continuous phase transition with signatures of criticality. Our experiments demonstrate mechanical properties consistent with our model, including the predicted critical exponents. We show that the nonlinear mechanics of collagen networks can be quantitatively captured by the predictions of scaling theory for the strain-controlled critical behavior over a wide range of network concentrations and strains up to failure of the material.

4.1 Introduction

As shown by Maxwell, networks of stiff rods that interact only through central-forces (i.e., tension or compression) exhibit a floppy to rigid phase transition at the \textit{isostatic} point, where the local coordination number, or connectivity \( z \) equals the threshold value of \( z_c = 2d \) in \( d \) dimensions [123]. At this point, the number of degrees of freedom is just balanced by the number of constraints, and the system is \textit{marginally stable} to small deformations. The jamming transition [157–161] of granular materials and rigidity percolation [162–165] of disordered spring networks are examples of such a transition. An important feature of these systems is the order of the transition. Jamming exhibits signatures of both first- and second-order transitions, with discontinuous behavior of the bulk modulus and continuous variation of the shear modulus [160, 166, 167]. For networks of springs or fibers, the floppy to rigid phase transition is continuous in both bulk and shear moduli [102, 113, 126, 160, 162, 168].

Interestingly, the open fibrous meshwork that provides structure and stability to cells and tissues usually have an average local connectivity below the central-force isostatic point. Collagenous networks in extracellular matrices are a good example of this: the local connectivity is between 3, corresponding to fiber branching, and 4, corresponding
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Figure 4.1: At zero strain networks undergo a continuous transition from floppy to rigid at the isostatic threshold \( z = z_c \). This connectivity threshold shifts to lower values for networks subject to shear strain \( \gamma \). This threshold defines a line \( \gamma_c(z) \) of continuous transitions. We study here strain-induced transitions indicated by the dashed arrow for a given \( z \) well below \( z_c \). The insets show SEM (Scanning Electron Microscope) images of reconstituted collagen networks indicating points of 3-fold and 4-fold connectivities. The scale bar is 200 nm. (SEM images by K.A. Jansen.)

To two distinct connected fibers. Typical collagen network connectivity is measured to be about 3.4, which makes these networks sub-isostatic with respect to both 2D and 3D isostatic thresholds [88, 122]. Sub-isostatic networks can, nevertheless, become rigid by means of other mechanical constraints such as fiber bending [100, 101, 113], or when they are subjected to external strain [145]. The threshold strain at which the transition occurs depends on the nature of the applied deformation (i.e., whether shear or extension), on the average connectivity of the network, as well as other structural properties [102]. However, the order of this strain-induced transition remains unclear.

In this chapter, we study the floppy to rigid transition of disordered sub-isostatic networks under simple shear. We show that these networks exhibit a line of second order transitions (Figure 4.1) at a strain threshold \( \gamma_c(z) \), for connectivities well below the isostatic threshold. Moreover, we demonstrate critical behavior along this line, specifically in the scaling properties of the mechanics, finite-size effects that reflect the underlying divergence of correlation lengths, as well as the expected critical slowing down in the network relaxation dynamics. We also show that these critical exponents differ from mean-field theory, yet are surprisingly insensitive to the spatial dimensionality and the global network structure. The nature of the applied deformation however, affects the dependence of the critical exponents on local connectivity. In particular, networks under simple shear yield exponents that evolve with \( z \) but are insensitive to \( z \) under isotropic expansion.
We test the relevance of these predictions in real materials and present experimental results from our close collaboration with K. Jansen and G. Koenderink [103] on reconstituted networks of type I collagen, the most abundant protein in mammals and a major structural component of most tissues [56]. Although collagen has been widely studied for many years, the mechanical properties of collagen matrices remain poorly understood. We find that collagen networks show evidence of critical behavior in their mechanical response to shear strain and that the shear modulus of these networks is in quantitative agreement with our model, including the predicted non mean-field critical exponents.

4.2 Models of Sub-isostatic Athermal Fiber Networks

4.2.1 Network construction

We model lattice-based networks in $d = 2$ and $d = 3$ dimensions as well as off-lattice Mikado networks in 2D, all with periodic boundaries to reduce any edge effects. For our lattice-based networks, fibers are arranged on a 2D triangular lattice or a 3D face-centered cubic (FCC) lattice with linear dimension $W$. In the 2D lattice, we randomly select two out of the three intersecting fibers at each vertex on which we attach a binary cross-link. This phantomization procedure enforces local 4-fold connectivity for the network. The third phantom fiber segment does not interact with the cross-linked segment pair [114]. Similarly, in 3D where there are 6 intersecting fibers at a vertex, we randomly select three distinct pairs of segments and form binary cross-links, again enforcing local 4-fold connectivity [115]. In both 2D and 3D, the average connectivity is further reduced from 4 by random dilution of bonds with probability $1 - p$, where $p$ is the probability of an existing bond. For our off-lattice network, we generate Mikado networks by random deposition of fibers in a 2D $W \times W$ box. A freely hinged cross-link is attached at the points wherever fibers intersect. Deposition continues until the desired average connectivity is reached [71, 101, 128]. These networks are sub-isostatic by construction, and are floppy in the absence of fiber bending [75, 113, 126] or other interactions [86, 102, 133].

4.2.2 Network elasticity

For small deformations, we stabilize our athermal sub-isostatic networks by enthalpic fiber bending. The fiber elasticity is characterized by both a stretching modulus $\mu$, and a bending rigidity $\kappa$. Together, they define a reduced dimensionless fiber rigidity $\tilde{\kappa} = \kappa/\mu l_c^2$, where $l_c$ is either the lattice spacing $\ell_0$ in lattice-based networks, or the typical mesh size in Mikado networks. The networks are subjected to an affine simple shear...
strain $\gamma$ or isotropic bulk expansion $\epsilon$ (Figure 4.2), and subsequently allowed to relax by minimization of the total elastic energy density. The total elastic energy density $U$, is calculated using a discrete form of the extensible wormlike chain Hamiltonian [70]

$$U = \frac{1}{V} \sum_f \left[ \frac{\mu}{2} \int_f \left( \frac{dl}{ds} \right)^2 ds + \frac{\kappa}{2} \int_f \left| \frac{d\hat{t}}{ds} \right|^2 ds \right],$$ (4.1)

where $V \propto W^d$ is the volume of the system, the terms in the square brackets represent the stretching and bending energy stored in a single fiber $f$ due to the local elongation $\frac{dl}{ds}$ and curvature $\left| \frac{d\hat{t}}{ds} \right|$, and the sum is performed over all the fibers in the networks. The stress and stiffness of the network are subsequently obtained by numerically evaluating the first and second derivatives of the minimized energy density with respect to the applied deformation, respectively.

The network stiffness, being proportional to the total elastic energy density, is a function of the applied deformation and the reduced bending rigidity $\tilde{\kappa}$, and it involves a summation over all fiber segments in the network. As such, the stiffness is naturally proportional to the total length of the fibers in a given volume, i.e., the line density $\rho$ [70, 71, 101]. Under simple shear, the network stiffness can be expressed by the tangent shear modulus

$$K = \mu \rho \tilde{K} (\gamma, \tilde{\kappa}, z),$$ (4.2)

where $\tilde{K}$ is a dimensionless function of the applied deformation, the reduced bending rigidity, as well as the connectivity. In a similar manner, the stiffness of a network under isotropic expansion is expressed by the bulk modulus $B = \mu \rho \tilde{B} (\epsilon, \tilde{\kappa}, z)$. 
4.2.3 Fiber rigidity and volume fraction

Consistent with previous computational studies [88, 103, 107], we report the stiffness (and stress) in units of $\mu \rho$. The line density $\rho$ is specific to the chosen network architecture. For lattice-based networks in $d$-dimensions, $\rho_d = \tilde{\rho}_d / l_c^{d-1}$, where $\tilde{\rho}_2D = \frac{6 \rho}{\sqrt{3}}$ and $\tilde{\rho}_{3D} = \frac{12 \rho}{\sqrt{2}}$ [107]. For Mikado networks, because of the polydispersity of $l_c$ it is more convenient to express the line density in terms of fiber length $L$ such that $\rho_M = \tilde{\rho}_M / L$, where $\tilde{\rho}_M = n_f L^2$ and $n_f$ is the number of rods per unit area [70]. With the appropriate normalization $\frac{K \mu \rho}{\mu \rho} = \tilde{K}$, this dimensionless modulus can be compared quantitatively with the stiffness as measured from experiments. To this end, we relate the reduced fiber rigidity to the total protein concentration $c$ via the volume fraction $\varphi$ of an arbitrary network geometry. Consider a 3D meshwork of homogeneous and monodisperse cylindrical fibers with uniform thickness. The volume fraction, which is a measure of the amount of fiber material per network volume, scales linearly with concentration. For an elastic rod of radius $a$ and Young’s modulus $E$, we know from classical beam theory [60] that $\mu = \pi a^2 E$ and $\kappa = \pi a^4 E / 4$. We also have the volume fraction $\varphi = \pi a^2 \rho \propto a^2 l_c^2 c$. The reduced fiber rigidity $\tilde{\kappa}$ is then naturally related to the total protein concentration in the experiments as follows. On substituting the expressions for $\mu$ and $\kappa$, we obtain $\tilde{\kappa} = \frac{a^2}{4E} \varphi \propto c$. Using these relations, we also obtain the normalization factor $\mu \rho = E \varphi$. Since $E$ is a material constant, it follows that $K / \varphi$ (or equivalently $K / c$) from experiments can be directly compared with $\tilde{K}$ from simulations. These relations have an important consequence from an experimental perspective: the magnitude of the modulus and stress as well as the functional dependence of the stiffness on the applied deformation is insensitive to the fiber thickness for a given concentration. This follows immediately on noting that the mesh size $l_c$ scales linearly with the fiber thickness for a given protein concentration since $\tilde{\kappa} \propto (a/l_c)^2 \propto \varphi$ is constant.

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4.3.1 Continuous rigidity transition

In Figure 4.3a, we show the network stiffness $K$ vs strain $\gamma$ of a 2D lattice-based network with $z = 3.4$ for different values of $\tilde{\kappa}$. As sketched in Figure 4.1 and as shown in Figure 4.3b, these networks are characterized by a continuous transition at a strain threshold $\gamma_c$, which is indicated in Figure 4.3a by the dashed red curve, above which the stiffness $K$ increases continuously from zero for $\tilde{\kappa} = 0$. This curve is approached for systems with finite but decreasing $\tilde{\kappa}$, as can be seen by the lower sets of curves. When $\tilde{\kappa} = 0$, fiber bending costs no energy and the stiffness remains zero for strains $|\gamma| \leq \gamma_c$. 

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Figure 4.3: (a) Stiffness $K$ in units of $\mu\rho$ vs strain $\gamma$ in a 2D lattice-based network with $z = 3.4$. The red dashed curve, starting from $\gamma = \gamma_c$, is a schematic of the stiffening curve expected from a sub-isostatic network with $\tilde{\kappa} = 0$ while the red solid curve is the affine limit with $\tilde{\kappa} = \infty$. The blue dash-dotted curve interpolates through the points on the stiffening curves that mark the strain $\gamma_0$ at the onset of nonlinearity. The inset is the $\tilde{\kappa}$-dependence of the linear modulus $G_0$ with the dashed line indicating a unit slope. (b) Critical strain $\gamma_c$ and the threshold strain $\gamma_0$ vs average connectivity for 2D lattice-based networks. The thick curves interpolate through the points and intersect $\gamma_c = 0$ at the isostatic threshold $z_c = 4$. As in Figure 4.1 The thick solid curve separates the floppy from the rigid phases.
Above $\gamma_c$, $K$ increases continuously from zero. The critical strain $\gamma_c$ is determined by the nature of applied deformation and the network architecture, in particular its average connectivity [102]. At the isostatic threshold $z_c = 2d$, a central force network is marginally stable with $\gamma_c = 0$. In Figure 4.3b, we show $\gamma_c$ versus $z$ when the network is subjected to simple shear deformation. For a given average connectivity below the isostatic threshold, increasing the deformation causes a floppy-to-rigid phase transition. In the absence of the stabilizing effect of fiber bending, i.e., for $\tilde{\kappa} = 0$, the continuous nature of the transition in $\gamma$ is apparent in the critical scaling of the network stiffness $K \sim |\Delta \gamma|^f$ in the regime where $\Delta \gamma = \gamma - \gamma_c > 0$ (Figure 4.4).

4.3.2 Analogy with the ferromagnetic transition

The strain-driven rigidity transition is well-defined only in the limit of $\tilde{\kappa} \to 0^+$ at which the interactions between the network fibers are governed purely by central force interactions. With the addition of a stabilizing field such as fiber bending, the network becomes stable for $\gamma < \gamma_c$, with the stiffness $K \propto \tilde{\kappa}$. This behavior is reminiscent of the continuous second-order phase transition of an order parameter in ferromagnetism.
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Figure 4.5: (a) Non-affine bending fluctuations $\Gamma_\theta$ obtained from simulations on a 2D lattice-based network with $z = 3.4$ and different $\tilde{\kappa}$, plotted vs strain. In the limit of $\tilde{\kappa} \to 0^+$, the rate of increase of fiber bending with respect to an infinitesimal $d\gamma$ diverges close to the critical strain $\gamma_c$ indicated by the arrow. (b) Differential non-affinity $\delta \Gamma$ obtained from the same simulations in (a). As in $\Gamma_\theta$, the height of the $\delta \Gamma$ peak increases as $\tilde{\kappa} \to 0^+$, since the displacement field becomes highly non-affine as $\gamma \to \gamma_c$ (indicated by the arrow). (c) Critical strain $\gamma_c$, obtained from simulations on a 2D lattice-based network with $z = 3.4$ as: the peak of $\Gamma_\theta$ (□), as the peak of $\delta \Gamma$ (○), and as the inflection point of the log $K$ vs. log $\gamma$ curves (△).

Ferromagnetic materials are characterized by a Curie temperature $T_c$ such that for temperatures $T > T_c$, the material is paramagnetic. Upon lowering the temperature past $T_c$, a spontaneous magnetization of the material occurs which increases continuously from zero as $M \propto |\Delta T|^\beta$, where $\Delta T = T - T_c < 0$ and $\beta$ is a critical exponent. Above the Curie temperature, the paramagnetic phase is characterized by zero magnetization. However, in the presence of an external finite magnetic field $H$, there is a net magnetization in the paramagnetic phase for which $M \propto H$. This is an intriguing analogy for the strain-driven transition: by mapping fiber rigidity $\tilde{\kappa}$ to the external field $H$, and deformation $\gamma$ to temperature $T$, one could study the transition of fiber networks from floppy to rigid states in a similar way as paramagnetic to ferromagnetic transitions.

4.3.3 Divergent non-affine fluctuations

We will show later that the analogy described above is quite useful in writing general constitutive relations for the nonlinear mechanics of the network. First, we need to verify certain signatures of criticality in the nonlinear mechanics of athermal sub-isostatic fiber networks. In critical phenomena associated with thermal systems, there are divergent fluctuations in the order parameter at the critical point. However, in our athermal networks, divergent fluctuations in the macroscopic observable $K$ do not exist. One could measure fluctuations by considering the deviations of the local deformation field in the network relative to the expected affine field. If the deformation field is affine, the fibers are only either stretched or compressed and do not undergo bending. The deviation from the affine field induces bending which can therefore be considered as a measure of these fluctuations. We define $\Gamma_\theta$ as a measure of the rate of change with the
applied strain at which bending develops in the network:

\[ \Gamma_\theta(\gamma) = \frac{\partial \langle \theta_{ijk}^2 \rangle}{\partial \gamma}, \]  

(4.3)

where \( \theta_{ijk} \) is the local bending angle between two consecutive segments \(((ij), (jk))\) on a fiber. The angular brackets is an average over all triplets \((ijk)\) in the network. An alternative but similar measure of fluctuations is the differential non-affinity, which measures the local strain fluctuations in the network. Given the displacement field \( u \) and the affine displacement field \( u^A \) of the network, the non-affine fluctuations can be quantified by the differential non-affinity [102]

\[ \delta \Gamma(\gamma) = \frac{\langle \|\delta u^{NA}\|^2 \rangle}{l_c^2 d\gamma^2}, \]  

(4.4)

where \( \delta u^{NA} = u - u^A \) is the differential non-affine displacement of a given point on the network resulting from an imposed strain \( d\gamma \), \( l_c \) is the typical network mesh size, and the angular brackets represent an average over all points in the network. We calculate both measures of fluctuations (Equation 4.3 and Equation 4.4) in the network for a range of fiber rigidities and study the behavior in the limit of \( \tilde{\kappa} \to 0^+ \). For finite \( \tilde{\kappa} \), we define the critical strain \( \gamma_c \) as the inflection point of the log \( K \) vs. log \( \gamma \) curves, analogous to the determination of the critical point in a finite size system [169]. In Figure 4.5a, we show \( \Gamma_\theta \) versus \( \gamma \) from simulations on a 2D lattice-based network. We note the shift in the peak of \( \Gamma_\theta \) towards smaller \( \gamma \) values as well as the increase in the peak height with decreasing fiber rigidity. The increasing peak height also indicates that the rate of fiber bending fluctuations increases rapidly with the applied strain near \( \gamma_c \). In Figure 4.5b, we show \( \delta \Gamma \) in the neighborhood of the critical strain. Similar to \( \Gamma_\theta \), the non-affine fluctuations grow with decreasing \( \tilde{\kappa} \). In the limit of \( \tilde{\kappa} \to 0^+ \), the position of
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Figure 4.7: (a) Strain-stiffening curves from a 2D lattice-based network with $z = 3.2$ and $\tilde{\kappa} = 10^{-7}$ for increasing system size. (b) Finite-size collapse of the stiffening curves according to Equation 4.5. The slope of the upper branch (thick black line) yields the critical exponent $f = 0.75 \pm 0.05$, while the correlation length exponent is $\nu = 2.0 \pm 0.1$. Here, the stiffening curves are shown for three bending rigidities approaching the $\tilde{\kappa} \rightarrow +0$ limit. The lower branch is asymptotic to level that scales with the bending rigidity. In the limit of $\tilde{\kappa} \rightarrow 0^+$, the lower branch drops all the way down to zero.

the peak coincides with our definition of the critical strain from the inflection point of the stiffening curves (Figure 4.5c). These observations of diverging fluctuations near the critical point as $\tilde{\kappa} \rightarrow 0^+$ (Figure 4.6) support our proposed mapping of fiber bending rigidity as an auxiliary field.

4.3.4 Finite-size scaling

Signatures of criticality in our model can be further tested by finite-size scaling analysis. Such analysis is sensitive to the divergence of the spatial extent (i.e., correlation length) of clusters of divergent fluctuations. In our system, the order parameter analog $K$ scales as $|\Delta\gamma|^f$ (Figure 4.4), as the system size $W \rightarrow \infty$ and $\Delta\gamma \rightarrow 0^+$. This scaling should be evident when the correlation length which scales as $|\Delta\gamma|^{-\nu}$, is much smaller than the system size, with $\nu$ being the correlation length exponent. At the critical point, the correlation length diverges and the modulus should scale with system size as $K \sim W^{-f/\nu}$, such that vanishes continuously as $W \rightarrow \infty$. These scaling relations can be summarized as follows:

$$K \sim W^{-f/\nu} F_{\pm} \left( |\Delta\gamma| W^{1/\nu} \right).$$

(4.5)

To test the above scaling, we choose a finite but small bending rigidity $\tilde{\kappa} \rightarrow +0$ to avoid the numerical problems associated with a network of rope-like fibers (i.e., $\tilde{\kappa} = 0$). These rope networks show a discontinuous jump in the energy density at $\gamma_c$ due to finite size effects. Since $K$ requires derivatives of energy density with respect to $\gamma$, it becomes numerically problematic to extract the order parameter at the critical point. The derivative becomes unambiguous only by taking $\tilde{\kappa} \rightarrow 0^+$. We show the stiffening
curves for $\tilde{\kappa} = 10^{-7}$ in Figure 4.7a for a 2D system with sizes ranging from $W = 40$ to $W = 200$. In Figure 4.7b, we collapse the stiffening curves using Equation 4.5. Except for the lower branch, the collapse is indistinguishable for the small values of $\tilde{\kappa}$ shown in the figure. The lower branch converges to an asymptote level that scales linearly with $\tilde{\kappa}$. This asymptote should therefore decrease continuously to zero as $\tilde{\kappa} \to 0^+$, consistent with an unstable central-force sub-isostatic network for $\gamma \leq \gamma_c$.

### 4.3.5 Crossover between elastic regimes

As mentioned above, in the absence of fiber bending, the network scales as $K \sim |\Delta\gamma|^f$ for $\Delta\gamma = \gamma - \gamma_c > 0$. For $\gamma < \gamma_c$, the network can be stabilized by fiber bending which leads to the $K \sim \tilde{\kappa}$ regime. These two regimes on either side of the critical strain can be summarized by the scaling form

$$K \sim \mu \rho |\Delta\gamma|^f \tilde{\kappa}^\pm \left( \frac{\tilde{\kappa}}{|\Delta\gamma|^\phi} \right), \quad \text{(4.6)}$$
where $K_{\pm}$ is a scaling function for which the positive and negative branches correspond to the regimes $\Delta \gamma > 0$ and $\Delta \gamma < 0$, respectively. This scaling is analogous to that of the conductivity of random resistor networks and the rigidity of fiber networks as a function of connectivity $z$ [113, 170], although the transition here occurs as a function of $\gamma$ rather than $z$ and $\Delta \gamma$ represents the distance from the critical line in Figure 4.1 or Figure 4.3b. We test the scaling in Equation 4.6 by plotting $K|\Delta \gamma|^{-f}$ vs. $\tilde{\kappa}|\Delta \gamma|^{-\phi}$ in Figure 4.6a. For $x \ll 1$, either $K_+(x)$ is approximately constant corresponding to the $K \sim |\Delta \gamma|^{-f}$ regime, or $K_-(x) \propto x$ corresponding to the $K \sim \tilde{\kappa}$ regime. At the critical point with $x \gg 1$, $K$ becomes independent of $|\Delta \gamma|$ and is nonzero and finite. As such, we expect $K \sim \kappa f/\phi \mu^{1-f/\phi}$. These three features are observed as three branches in the collapse of the stiffening curves shown in Figure 4.8, consistent with (4.6). To show the generality of this result, we plot in Figure 4.8 the data obtained from 2D and 3D lattice-based networks with the same connectivity $z = 3.3 \pm 0.1$. We also show data from Mikado networks with $z = 3.6$ as well as a 2D lattice-based network with $z = 3.4$. Interestingly, the slope $f/\phi$ of the critical branch seems to change with $z$. Even more interesting is that networks with the same connectivity collapse with the same exponent $f/\phi = 0.36 \pm 0.01$, independent of dimensionality.

4.3.6 Evidence of crossover from collagen networks

To test these predictions for a biologically relevant system, we polymerize networks of collagen type I at $37^\circ$C and at $30^\circ$C for a range of concentrations (Appendix A) and plot the strain stiffening curves in Figure 4.9a and Figure 4.9b. We also measured the average connectivity of these networks to be $z = 3.3 \pm 0.1$ from scanning electron microscopy (SEM) images (Appendix A) shown in Figure 4.9c and Figure 4.9cd, which is consistent with measurements from a previous study [122], as well as falling within the range of $z$ that we use in our simulated networks. Both confocal reflectance and SEM images show that networks polymerized at $37^\circ$C and $30^\circ$C are homogeneous. The images obtained by SEM are consistent with the qualitative observation that the fibers are thinner and more numerous at $37^\circ$C than at $30^\circ$C. These findings are in agreement with previous studies on collagen, where a decrease in mesh size as determined by confocal imaging was correlated with both a decrease in mesh size and increase in fiber diameter as determined by SEM [64, 171, 172]. We do note, however, that the diameter one obtains from SEM is likely to be different from the diameter in the hydrated state due to loss of water [173]. Nevertheless, we think that SEM imaging conserves the network structure (i.e., connectivity), even though the pore size and fiber thickness are likely different from the hydrated state. Furthermore, we note that the average $z$ determined by SEM is in excellent agreement with earlier measurements in collagen [122].
Figure 4.9: (a) Confocal reflectance microscopy images of collagen networks prepared at a concentration of 4 mg/mL and \(T = 37^\circ C\) and (b) at \(T = 30^\circ C\). Scanning electron microscopy (SEM) images of the same networks are shown in (c) and (d), respectively revealing the microstructure of the networks at 50,000× magnification. The branched structure of the collagen fibers is visible. The scale bar in (a) represents 20 µm for the confocal images, while the scale bar in (c) denotes 1 µm for the SEM images. (Images by K.A. Jansen.)

Figure 4.10a shows a series of measurements of the stiffness of collagen networks polymerized at \(37^\circ C\) as a function of strain for concentrations between 0.7 and 5.0 mg/mL. As discussed in Section 4.2.3, our model accounts for fiber thickness, mesh size and concentration through the parameter \(\tilde{\kappa}\), which is predicted to increase linearly with protein concentration \(c\) \[152, 174\]. By rescaling \(K\) with concentration, we can compare directly with the predicted collapse in Figure 4.8. As in our simulations, we extract \(\gamma_c\) from the inflection point of the log \(K\) vs. log \(\gamma\) curves. From these considerations, our model predicts that the stiffness should be governed by the scaling relation

\[
\frac{K}{c} \propto |\Delta \gamma|^f \kappa_\pm \left( \frac{c}{|\Delta \gamma|^\phi} \right).
\]

We test this prediction by plotting \(\frac{K}{c}|\Delta \gamma|^{-f}\) vs \(c|\Delta \gamma|^{-\phi}\) in Figure 4.10b. We find an excellent collapse using our predictions for the 3D networks shown in 4.8, by imposing the exponents \(f = 0.8\) and \(\phi = 2.1\) in collapsing the experimental data. Moreover,
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Figure 4.10: (a) Nonlinear stiffness vs strain measured up to the point of sample rupture (up to about 30-50%) for collagen networks prepared at 37°C for different concentrations (in mg/mL, increasing gray level): 0.7 (\(\triangle\)), 1.0 (\(\triangledown\)), 2.0 (\(\triangleleft\)), 3.0 (\(\bigodot\)), 4.0 (\(\bigotimes\)) and 5.0 (\(\bigbox\)). Three measurements are shown for each concentration. The inflection points that define the critical strain \(\gamma_c\) are in each case marked by red symbols, while the strain threshold at the onset of nonlinear stiffening are marked in blue. The inset shows the concentration scaling of the linear modulus with the dashed line indicating our model prediction \(G_0 \sim c^{2.2}\) for comparison. (b) Collapse of the stiffening curves in (a) according to Equation 4.7 with \(f = 0.8\) and \(\phi = 2.2\). The inset shows a weak dependence of \(\gamma_c\) on concentration, with the dashed line representing the model prediction \(\gamma_c \sim c^{-0.08}\) and is not a line of best fit. (c) Same plot as in (a) for networks polymerized at 30°C for concentrations (in mg/mL, increasing gray level): 2 (\(\triangle\)), 3 (\(\bigodot\)), 4 (\(\bigotimes\)), and 5 (\(\bigbox\)). The inset shows the model prediction \(G_0 \sim c^{2.1}\) compared with the data. (d) Collapse of the stiffening curves in (c) according to Equation 4.7 with \(f = 0.8\) and \(\phi = 2.1\). The dashed line in the inset is not a best fit but a comparison with the model prediction \(\gamma_c \sim c^{-0.08}\) (Experimental data by K.A. Jansen.)
experiments on collagen networks prepared at 30°C (Figure 4.10c) are also consistent with our model predictions (Figure 4.10d) implying the generality of our observations of criticality.

4.3.7 Crossover function and model fitting

In contrast to prior empirical rescaling of rheology data by sample-dependent characteristic values of stress and strain [108, 175], our observation of criticality allows us to determine an analytic expression for the nonlinear mechanics of collagen networks over the entire strain range in terms of the scaling function $K_\pm(x)$. To achieve this, we utilize the analogy with the paramagnetic-ferromagnetic phase transition. In ferromagnetism, the magnetization $m$ as a function of reduced temperature $t = (T - T_c)/T_c$ and in the presence of an external magnetic field $h$ can be captured by the following scaling relation [176]:

$$
\frac{h}{|t|^\Delta} \sim \frac{m}{|t|^\beta} \left( \pm 1 + \frac{m^{1/\beta}}{|t|} \right)^{(\Delta - \beta)}. \tag{4.8}
$$

Here, the $(\pm)$ branch corresponds to $t \gtrsim 0$, and $\Delta$ and $\beta$ are the critical exponents. The analogous quantities for the strain-driven rigidity transition of a fiber network are the following:

$$
\Delta \leftrightarrow \phi \\
\beta \leftrightarrow f \\
\frac{h}{|t|^\Delta} \leftrightarrow \frac{\tilde{k}}{|\Delta\gamma|^\phi} \\
\frac{m}{|t|^\beta} \leftrightarrow \frac{K}{|\Delta\gamma|^f}
$$

Based on this analogy, we write the following scaling relation:

$$
\frac{\tilde{k}}{|\Delta\gamma|^\phi} \sim \frac{K}{|\Delta\gamma|^f} \left( \pm 1 + \frac{K^{1/f}}{|\Delta\gamma|} \right)^{(\phi - f)}. \tag{4.9}
$$

Indeed, at the critical point $\Delta\gamma = 0$, the above scaling correctly reproduces $K \sim \tilde{k}^{f/\phi}$.

The stiffness $K$ as a function of strain $\gamma$ can be solved numerically from Equation 4.9 with $\tilde{k}$, $f$, $\phi$ and $\gamma_c$ as free parameters. However, one only requires the fiber rigidity $\tilde{k}$ as input. The critical strain $\gamma_c$ can be independently determined either from the onset of rigidity in a pure rope network or from the inflection point of the log $K$ vs. log $\gamma$ in the case of finite $\tilde{k} \rightarrow 0$ networks (Figure 4.5c and inset of Figure 4.10b,d). The critical exponents are also independently obtained from the data collapse using Equation 4.6 (Figure 4.8 and Figure 4.10b,d). In the linear regime, we know from simulations that the modulus $G_0$ (in
4.3 Strain-driven Criticality under Simple Shear

Figure 4.11: Nonlinear stiffness vs. strain measured for collagen networks prepared at 37°C for different concentrations (upper legend set). The inflection point at $\gamma_c$ is in each concentration indicated by red symbols. The dashed lines are the prediction of Equation 4.9, with each color a different value of the fit parameter $\tilde{\kappa}$ (lower legend set). For each concentration, three different sample measurements were performed (see Figure 4.10a). The values of $\tilde{\kappa}$ used to fit Equation 4.9 through the data are shown in the inset on a linear scale. The average value for each concentration is shown as filled red circles. The linear scaling of $\tilde{\kappa}$ with the concentration $c$ is consistent with the predictions of our model. (Experimental data by K.A. Jansen.)

units of $\mu_p$) scales linearly with $\tilde{\kappa} \sim \rho$, giving rise to the quadratic scaling with protein concentration: $G_0 \sim c^2$ (i.e., $G_0 \sim \rho^2$). However, from our empirical observations in the inset of Figure 4.10a and Figure 4.10c, the linear modulus shows $G_0 \sim c^{2+\delta}$ scaling. Because of this deviation, the numerical fitting procedure we describe here as applied to experimental data therefore needs to be slightly modified in the following way. We first rescale the modulus by $c^{1+\delta}$ such that $\frac{G_0}{c^{1+\delta}} \sim c \sim \tilde{\kappa}$. We then take the stiffening curve for a specific concentration, appropriately rescaled by $c^{1+\delta}$ and fit Equation 4.9 through the data using the appropriate $\gamma_c$ obtained from the inflection point. In this procedure, the only fit parameter is the fiber rigidity $\tilde{\kappa}$. The numerical fits are shown in Figure 4.11 superimposed on the experimental data. Different measurement samples for a given concentration are also fitted independently. In the inset of Figure 4.11, the average values of the free parameter $\tilde{\kappa}$ as obtained from fitting three samples per concentration scales linearly with $c$, consistent with our model predictions.
Figure 4.12: (a) The strain at the onset of stiffening scales as $\gamma_0 \sim \gamma_c^{(\phi-f)}$ in our 2D lattice-based networks. The inset shows the linear scaling of stress with $\tilde{\kappa}$ at the onset of stiffening. (b) The same scaling $\gamma_0 \sim \gamma_c^{(\phi-f)}$ is observed for collagen networks polymerized at different temperatures for the range of concentrations considered in the experiments. This scaling is a direct consequence of the $c^2$ scaling of the shear stress at $\gamma_0$ as shown in the inset. (Experimental data by K.A. Jansen.)

Although it is plausible that the deviation $\delta$ is due to experimental uncertainty, it is possible that the weak concentration dependence of the critical strain could account for it. In a recent study, it was shown that the threshold strain $\gamma_0$ at the onset of stiffening is independent of collagen concentration, with invariance to network architecture suggested as the underlying reason [88, 107]. Being a strain that characterizes the nonlinear regime, the same argument should also hold for the critical strain. However, on plotting $\gamma_c$ versus concentration, a rather weak dependence on concentration is apparent (inset, Figure 4.10b,d). It is possible that with increasing concentration, the average network connectivity increases leading to a slight decrease in $\gamma_c$. In the linear regime, by taking the limit $\gamma \to 0$, we expect from Equation 4.6 the following scaling of the linear modulus with concentration: $\frac{G_0}{c} \sim c^{\gamma_c^{(f-\phi)}}$. This accounts for the apparent deviation in the lower branches of Figure 4.10b and Figure 4.10d: $\frac{G_0}{c} \sim c^{\gamma_c^{(f-\phi)}} \sim c^{1+\delta}$ leading to the weak concentration dependence of the critical strain $\gamma_c \sim c^{\delta(f-\phi)} \sim c^0$. Indeed, the exponent $\eta = \frac{\delta}{f-\phi}$ for collagen networks prepared either at $T = 37^\circ C$ ($\eta \simeq -0.14$) or $T = 30^\circ C$ ($\eta \simeq -0.08$) provides evidence that network connectivity evolves weakly with concentration.

We further confirm the internal consistency of the critical exponents by relating the strain threshold $\gamma_0$ with $\gamma_c$. An expression for $\gamma_0$, based on geometrical arguments has been derived in [107]. We also expect from the model that at the onset of stiffening, the stress $\sigma_0 \sim G_0 \gamma_0 \sim \tilde{\kappa}$ (inset, Figure 4.12a). From Equation 4.6, we obtain in the linear regime $G_0 \sim \tilde{\kappa} \gamma_c^{(f-\phi)}$. It follows that $\gamma_0 \sim \gamma_c^{(\phi-f)}$ as shown in Figure 4.12a. This scaling is confirmed by experiments, where $\sigma_0 \sim G_0 \gamma_0 \sim c^2$ (inset, Figure 4.12b). From 4.7, $G_0 \sim c^2 \gamma_c^{(f-\phi)}$, and we obtain $\gamma_0 \sim \gamma_c^{(\phi-f)}$ as shown in Figure 4.12b. Unlike $\gamma_0$, which can be determined analytically, determination of $\gamma_c$ from this scaling argument requires
the knowledge of the critical exponents which, at present, are only obtained from the collapse of the strain-stiffening data.

### 4.3.8 Evolution of critical exponents

The critical exponents obtained from the data collapse in Figure 4.8 from simulations are similar to the exponents used to collapse the experimental data in Figure 4.10. Apparently, the exponents are independent of dimensionality when the networks under consideration have the same connectivity. This is in contrast to critical phenomena of thermal systems as in ferromagnetism [177] and the liquid-vapor transition [178] as well as nonthermal criticality in percolation [169]. In such systems, the critical exponents depend on the spatial dimensionality. In the strain-driven rigidity transition of fiber networks, the critical exponents evolve with the average connectivity. In Figure 4.13a, we show the nonlinear stiffness data collapsed according to Equation 4.6 for 2D lattice-based networks prepared within the range of connectivities straddling the experimentally relevant values for collagen networks. It is clear that $f$ increases with the average connectivity while $\phi$ remains practically constant.

<table>
<thead>
<tr>
<th>$\langle z \rangle$</th>
<th>Network</th>
<th>$f$</th>
<th>$f/\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>2d Honeycomb</td>
<td>0.50</td>
<td>0.22</td>
</tr>
<tr>
<td>3.2</td>
<td>2d phantom</td>
<td>0.75</td>
<td>0.36</td>
</tr>
<tr>
<td>3.2</td>
<td>3d phantom</td>
<td>0.80</td>
<td>0.36</td>
</tr>
<tr>
<td>3.6</td>
<td>2d Mikado</td>
<td>0.84</td>
<td>0.38</td>
</tr>
<tr>
<td>5.0</td>
<td>3d FCC</td>
<td>1.45</td>
<td>0.50</td>
</tr>
</tbody>
</table>

In Table 4.1 we summarize the various values of $f$ and $f/\phi$ for different network structures in either 2D or 3D. Although the theoretical results above were chosen to correspond to connectivities close to the experimental values for collagen networks, we also studied two very different networks: a disordered honeycomb lattice in 2D (Appendix B) with $z$ close to 2 showing a good collapse with $f/\phi \simeq 0.22$ (inset, Figure 4.13b) and a diluted 3D FCC lattice with $z$ close to the isostatic point (Figure 4.13a). Importantly, the near-isostatic network shows $f/\phi \simeq 1/2$, consistent with the $K \sim \kappa^{0.5}$ scaling reported in Ref. [113] for an isostatic network. We note however, that the individual exponents $f$ and $\phi$ here are only defined for sub-isostatic networks, and thus are not expected to coincide with studies of isostatic systems [113, 126].

Although, we do not have a theoretical understanding of the evolution of the exponents with the average connectivity, it is interesting to experimentally verify an important consequence of such an evolution. In order to do so, the connectivity in a network needs
Figure 4.13: (a) Strain-stiffening curves collapsed according to the Equation 4.6 for 2D lattice-based networks for different connectivities (see legend) and for the fiber rigidities as shown in Figure 4.8. In the inset, we show a significant evolution of the exponent $f$ with connectivity for 2D lattice-based networks. The ratio $f/\phi$ also increases with $z$, with $2.0 < \phi < 2.2$ showing practically no dependence. (b) Similar collapse from a 3D lattice-based network with $z \approx 5$. For this near-isostatic network (i.e., $z \lesssim 6$), the critical exponents are $f = 1.45$ and $\phi = 2.9$. The ratio $f/\phi \approx 1/2$ is consistent with the scaling $K \sim \kappa^{0.5}$ reported in [113] for an isostatic network in 3D. The inset shows the data collapse from a 2D disordered honeycomb lattice at the far lower end of connectivities ($z = 2.4$) using $f = 0.48$, $\phi = 2.2$. 

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Chapter 4 Mechanically-controlled criticality in fiber networks
4.4 Nonlinear Mechanics under Isotropic Expansion

to be systematically tuned. We have seen that the average connectivity shows a very weak dependence on the concentration. Tuning network connectivity with concentration, though possible, is not a very practical method to verify the evolution of $f$ with $z$. In an isotropic network, the total number of constraints increase with the degree of connectivity. It has been shown that a sub-isostatic isotropic network, when subjected to isotropic compression, resembles a network with an effective reduced connectivity [102]. The main effect of isotropic compression is to delay the onset of stiffening. Under compression, although the network connectivity remains same, the number of constraints are effectively reduced by introducing more fiber undulations. Likewise, isotropic extension should increase the number of constraints. It is interesting therefore, to test the evolution of the critical exponent in experiments by subjecting the networks to either compression or extension before applying shear deformation. According to our model, we expect the exponent $f$ to decrease with compression and increase with extension.

4.4 Nonlinear Mechanics under Isotropic Expansion

The perspective of critical phenomena provides a theoretical framework for the nonlinear mechanics of athermal fiber networks consistent with experiments on collagen under shear. This is particularly satisfying given the fact that volume preserving shear deformation is biologically the most relevant one [179–182]. However, from a theoretical perspective, it is interesting to generalize this framework to other deformations such as isotropic extension. In fact, it is an interesting question as to whether the theoretical approach can be applied for a generalized deformation tensor. However, we believe that there is only a limited subset of deformations that can be captured within our framework of critical phenomena. Only those deformations which can stabilize an otherwise floppy network, by eventually invoking stretching modes (i.e., central force interactions) can drive mechanical critical behavior. For instance, a sub-isostatic network with only central force interactions cannot be stabilized by isotropic compression. In contrast, under isotropic extension, the same network becomes rigid at a critical strain $\epsilon_c$ [102]. For isotropic deformations, we define the bulk modulus $B(\epsilon) = \frac{n}{d^2} \frac{\partial^2 \mathcal{H}(\epsilon)}{\partial \epsilon^2}$ as in [102], where $\mathcal{H}$ is the average elastic energy per bond, $n$ is the density of bonds in the network, and $d$ is the dimensionality. The density is defined based on the initial unstrained network size. As with simple shear, we consider the following questions. (1) Does the stiffness of a sub-isostatic network when subjected to isotropic expansion exhibit a critical scaling as $B \sim |\epsilon - \epsilon_c|^f$? (2) Are the critical exponents $f$ and $\phi$ for isotropic extension the same as for shear for a fixed network connectivity? (3) Are the exponents independent of the spatial dimensionality? (4) Do the exponents evolve with the degree of connectivity?
Figure 4.14: (a) Bulk stiffness versus strain obtained from a 2D lattice-based network with $z = 3.2$ subject to isotropic expansion. Blue dashed lines through the symbols are predictions of Equation 4.9 with $\Delta \gamma$ replaced by $\Delta \epsilon$ and with the critical exponents $f = 0.35$ and $\phi = 2.0$. (b) Data in (a) collapsed according to Equation 4.10 shown in black. Bulk stiffness data from a 3D lattice-based network with the same connectivity as in the 2D data is shown in red. The critical exponents are independent of spatial dimensionality: $f = 0.35$ and $\phi = 2.0$. 

4.4 Nonlinear Mechanics under Isotropic Expansion

Figure 4.15: Collapse of strain-stiffening curves according to Figure 4.10 obtained from a 2D lattice-based network with connectivities $z = 3.4$ (black), $z = 3.6$ (blue) and $z = 3.8$ (red). For these connectivities, the critical exponents are the same: $f = 0.35$ and $\phi = 2.0$. Here, the data has been shifted vertically by an arbitrary value to distinguish the different datasets. The dashed line has slope given by $f/\phi$, while the solid line has a unit slope.

We first test the critical scaling of the stiffness. Analogous to Equation 4.6, stiffness of a network under isotropic extension can be written as:

$$B \propto |\Delta \epsilon|^f B_{\pm} \left( \frac{\tilde{\kappa}}{|\Delta \epsilon|^\phi} \right),$$

(4.10)

where $\Delta \epsilon = \epsilon - \epsilon_c$, $f$ and $\phi$ are the critical exponents associated with the isotropic expansion and $B$ is the crossover function. In Figure 4.14a we show the stiffness $B$ versus $\epsilon$ for different values of $\tilde{\kappa}$ of a 2D triangular lattice network with $z \approx 3.2$. The stiffness curves collapsed according to Equation 4.10 are shown in Figure 4.14b. The critical exponents obtained are $f = 0.35 \pm 0.05$ and $\phi = 2.1 \pm 0.1$. Whereas $\phi$ is practically the same as in simple shear, $f$ is significantly smaller. Furthermore, as in simple shear, the exponents appear to be independent of spatial dimensionality as data from a 3D lattice-based network under isotropic expansion likewise collapses with the same set of exponents with the 2D data (Figure 4.14b). Interestingly however, in contrast to shear, the critical exponents appear to be rather insensitive to the network connectivity (Figure 4.15).
Figure 4.16: Reduction in elastic energy with time for two different network connectivities, \( z = 3.6 \) (red) and \( z = 3.2 \) (black) for isotropic expansion (a) and simple shear (b). Energy is expressed in units of the initial energy \( H_0 \) in the network just after the affine deformation. Time is expressed in arbitrary units, chosen to be same for both connectivities. Very near the critical strain, the relaxation dynamics scale as a power-law \( H \sim t^{-1} \) indicated by the thick blue line of \(-1\) slope for both isotropic expansion and shear. The critical slowing down exponent is insensitive to connectivity. Also shown for comparison are networks subjected to \( \pm 1\% \) of the critical strain values.
4.5 Critical Slowing Down

One of the hallmark signatures of critical phenomena is extremely slow dynamics at the critical point. The dynamics are characterized by a divergent relaxation time scale. We investigate critical slowing down in a disordered fiber network by subjecting it to an affine shear or isotropic deformation equal to the critical value. We then allow the network to relax the elastic energy by performing overdamped molecular dynamics simulations. We neither take hydrodynamics into account nor the asymmetric nature of drag acting on each fiber. We rather assume that the forces acting on the network due to the surrounding solvent can be modeled as a simple Stoke’s drag which acts on any given point on the network. This is admittedly a highly simplified version of network dynamics. However, as shown in Figure 4.16 at the critical strain, the slow dynamics are robustly captured in the power law scaling of the total elastic energy in the network as a function of time. For longer times, the elastic energy stored in the network decays as \( H \sim t^{-1} \) at \( \epsilon = \epsilon_c \). This inverse-time decay is apparent in all the connectivities considered for isotropic expansion. In the case of simple shear, the same power-law dynamics are observed at the critical strain \( \gamma = \gamma_c \) with the same exponent of \( \approx -1 \). The exponent does not evolve with connectivity, regardless of the nature of the applied deformation. Slightly above and below the critical strain, the relaxation time scale becomes finite. The divergent relaxation time scale at the critical point originates in the highly delocalized fiber rearrangements in the network. These rearrangements are precisely associated with the deviation from the affine deformation field and are apparent as the divergent non-affine fluctuations (Figure 4.5a,b). In the thermodynamic limit, with \( W \to \infty \), the non-affine rearrangements grow without bound giving rise to the divergent time scale for energy relaxation.

4.6 Discussion and Conclusions

In this study, we have focused on the mechanical critical behavior in fiber networks. The criticality is driven by the applied deformation and is the fundamental mechanism for the nonlinear mechanics of such networks. The networks considered are athermal, disordered, and are by construction, sub-isostatic. We take into account two types of interactions: central force as in a Hookean spring and fiber bending. It is important to note that unlike the isostatic threshold which depends on the precise balance of the number of constrains to the degrees of freedom, any generic sub-isostatic network exhibits critical behavior. Signatures of criticality are evident in the neighborhood of the critical strain which is determined by the network architecture as well as the nature of the applied deformation. However, not all types of deformations drive such critical
behavior, thus preventing the generalization of criticality when considering an arbitrary deformation as a strain tensor. A perfect example is a sub-isostatic network governed by pure central force interactions and subjected to isotropic compression.

One of the hallmark features of critical phenomena is the power-law scaling of the order parameter in the vicinity of the critical point. We show that the network stiffness scales as a power-law, $K \sim |\Delta \gamma|^f$, where $\Delta \gamma$ is the “distance” from the critical strain and $f$ is a critical exponent. At the critical strain, the deformation field becomes highly inhomogeneous. Near the critical strain, the network response becomes highly nonlinear for small perturbations to the applied deformation, with particle displacements on the network deviating significantly from the affine field. The total strain fluctuation, quantified as the network average of the difference between the true and affine displacements, exhibits a very sharp peak at the critical strain. Moreover, network stiffness at the critical strain exhibits standard finite size scaling which is a manifestation of an underlying divergent correlation length.

Though naturally occurring networks in biology are structurally sub-isostatic, they are stable in the sub-critical regime due to additional interactions besides pure central forces. For example, in the presence of finite fiber bending, the network stiffness exhibits a crossover from bend-dominated elasticity in the sub-critical regime into a stretch-dominated regime above the critical point. From the perspective of critical phenomena, fiber bending rigidity can be considered as an auxiliary field that modulates diverging fluctuations at the critical strain. In fact, one expects the stiffness at the critical strain, to scale as a power-law with the relative strength of bending to stretching interactions. Drawing analogy with ferromagnetic phase transitions, in the presence of an auxiliary applied magnetic field $h$, we capture the bend-stretch crossover of stiffness in terms of a universal scaling function. An approximate equation for the scaling function is also derived, which we demonstrate to be highly accurate in describing the entire nonlinear strain-stiffening curves for any given bending rigidity. By mapping protein concentration to the reduced fiber rigidity, our model can accurately describe the strain-stiffening of reconstituted collagen networks with only a single fit parameter.

A surprising result in our model is that under simple shear, the critical exponents $f$ and $\phi$ appear to be independent of the spatial dimensionality: as long as networks have the same average connectivity, they yield the same critical exponents. However, the exponents are not constant as they appear to change with network connectivity. In particular, the exponent $f$ increases with connectivity, while $\phi$ remains practically constant. This is a highly intriguing and yet puzzling observation. The critical exponents, as is known from the theory of critical phenomena, depend on the spatial dimensionality. It becomes even more interesting when considering the critical exponents of a network.
subjected to isotropic expansion. Under isotropic expansion, the critical exponents do not depend on the spatial dimensionality as in simple shear. However, unlike shear, the exponents appear to be constant. The same scaling relation used to predict the stiffening curves for simple shear can also accurately predict isotropic expansion strain-stiffening. As expected, we see evidence of critical slowing down in the neighborhood of the critical strain when the network is subjected to either simple shear or isotropic expansion. The temporal behavior of the total elastic energy decays as power-law $\mathcal{H} \sim t^{-1}$ for long times. Such slow dynamics is independent of network connectivity.
4.7 Appendix A: Materials and Methods

For our experiments, rat-tail collagen type I (BD Biosciences, Breda) was polymerized at $T = 30^\circ C$ and $T = 37^\circ C$, in a physiological buffer solution composed of DMEM1x solution (diluted from 10x, Sigma) containing 50 mM HEPES, 1.5 mg/mL sodium bicarbonate, 1% FBS (Gibco) and 0.1% antibiotics (pen/strep, Gibco) at pH 7.3. Rheology was performed on a stress-controlled rheometer (Physica MCR 501; Anton Paar, Graz, Austria) with a 40 mm cone-plate geometry having an 1 degree cone angle. A solvent trap was added to maintain a humid atmosphere. After 6 hours polymerization, stiffness vs. stress curves were obtained using a differential protocol.

For scanning electron microscopy (SEM) imaging, collagen gels (50-100 $\mu$L) were polymerized overnight in 5 mL eppendorf tubes in humid conditions. After polymerization, samples were washed three times with sodium cacodylate buffer (50 mM cacodylate, 150 mM NaCl, pH 7.4) for 30-60 min each, at their polymerization temperature. Samples were fixed with 2.5% glutaraldehyde in the same buffer for at least 2 hours. The samples were then washed three times with sodium cacodylate buffer at room temperature and dehydrated with increasing percentage of ethanol. After complete dehydration (100 % ethanol), 50 % hexamethyldisilazane (HMDS) in ethanol was added (under the hood) and afterwards replaced after 30 min by 100% HMDS. The HMDS was left to evaporate overnight. The samples were transported to a stub with carbon tape and sputter coated using a K575X sputter coater (Quorum Technologies, Gouda, The Netherlands). A layer of 15.4 nm of Au/Pd was sputtered using a current of 80 mA. The SEM samples were visualized using a Scanning Transmission Electron Microscope (STEM) setup (Verios 460, FEI Company, Eindhoven, the Netherlands) using 50 pA, 5 kV and 4 mm working distance, in immersion mode. The connectivity was determined manually on SEM images with 20,000-50,000 times magnification. The images were divided by a grid of 5x5 squares and in every other square all junctions were taken into account. Per sample, a total of at least 100 junctions were counted. The average connectivity of a collagen network at both 37$^\circ$C and 30$^\circ$C was determined to be 3.3 ± 0.1.

To verify that the SEM preparation does not influence the network architecture, we imaged 4 mg/mL collagen networks in the hydrated state using confocal reflectance microscopy. The images were collected using an inverted Eclipse Ti microscope (Nikon) using a 488 nm Ar laser (Melles Griot, Albuquerque, NM) for illumination. We obtained z-stacks by recording confocal slices over a total distance of 20 $\mu$m with 0.2 $\mu$m z-spacing using a 100x (N.A. 1.49) oil objective, starting at least 10 $\mu$m away from the coverslip surface. For display purposes, the confocal stacks were summed to give an impression of the 3D network structure and the typical mesh size.
In the models described in this chapter, especially for the lattice-based networks, it is possible to generate branched architectures by random dilution until $z = 3.0$ is obtained. However, it is known that in branched biopolymer networks such as collagen, the fibers themselves consist of multiple fibrils which have internal covalent cross-links. The point at which two fibers seem to connect, is where the bundle of fibrils split up and combine to form branch points [183] (Figure 4.17a). High-resolution images of collagen reported in [184] show clear evidence for this feature. To generate branched network architectures, we use distorted honeycomb lattices with random bond dilution [185]. A schematic of a distorted honeycomb lattice is shown in Figure 4.17b. Note that as a consequence of the distortion, one obtains a network with a polydisperse bond rest length $\ell_{ij}$. The network elasticity is calculated as a sum of stretching and bending contributions from all bonds. The stretching energy of each bond is calculated in the same manner as in the 2D triangular lattice- or 3D FCC lattice-based networks, i.e.,

$$
H_{honeycomb}^{(i)} = \frac{\mu}{2} \sum_{(ij)} \ell_{ij} \left( \frac{\delta \ell_{ij}}{\ell_{ij}} \right)^2 .
$$

**Figure 4.17:** (a) Collagen is made up of long running fibrils that are internally cross-linked to form a single bundle which occasionally splits and branches out. The split bundles are consequently bent and therefore must store bending energy. (b) There are three bond pairs at every branch point. In the model, we assign a finite bending rigidity to each pair, except for one with the smallest angle which is assigned $\kappa = 0$. (c) A diluted honeycomb lattice with vertices distorted up to a maximum distance $d_{\text{max}} = 0.8\ell_0$, where $\ell_0$ is the bond length of the undistorted honeycomb lattice. (Schematic and network by R. Rens.)
The bending term however, is modified to capture the manner in which the fibers share bending energy at the junction. In discrete form,

$$\mathcal{H}_{\text{honeycomb}}^{(b)} = \sum_{\langle ijk \rangle} \frac{\kappa_{ijk}}{(\ell_{ij} + \ell_{jk})} (\theta_{ijk} - \theta_{0,ijk})^2,$$

where $\langle ijk \rangle$ refers to a pair of consecutive segments in the network. For any pair there is a bending rigidity $\kappa_{ijk}$. At a given branch point we take $\kappa_{ijk} = \kappa$, except for the smallest angle for which we set $\kappa_{ijk} = 0$ (Figure 4.17c). Similar to the other network models, this modification of the bending energy in the case of branched structures shows a linear response to the change in the bending angle $\theta_{ijk}$ with respect to the initial branching angle $\theta_{0,ijk}$. 