# Flory-Huggins theory

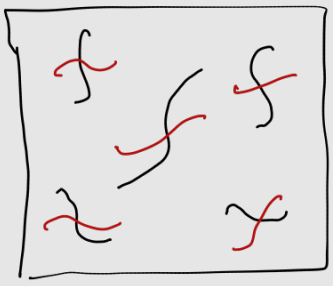
FH parameter ← fluctuation?

$$F_{mix} = k_B T \left[ \frac{\phi \ln \phi}{N_A} + \frac{(1-\phi)\ln\phi}{N_B} + \chi\, \phi(1-\phi) \right]$$

(per mon)

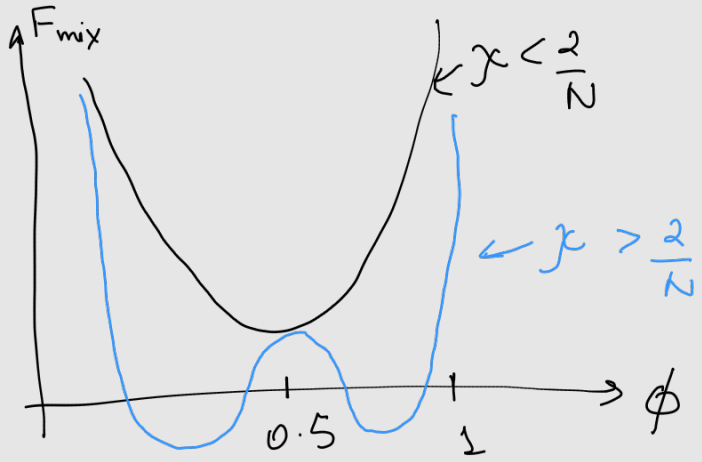
entropy

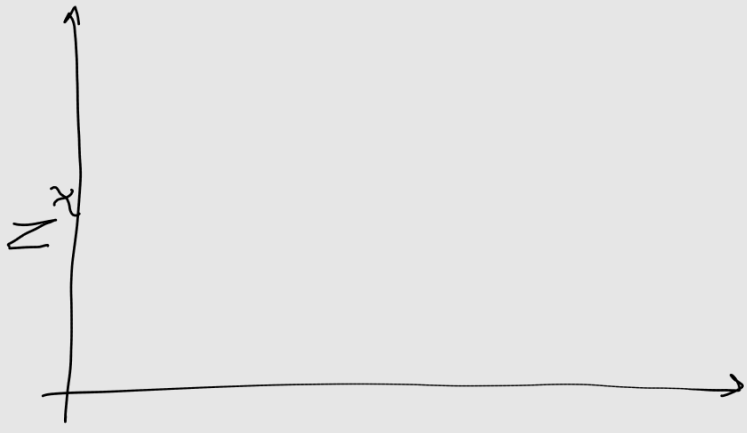
interactions.



$\phi_A + \phi_B = 1$

$\phi = \phi_A$



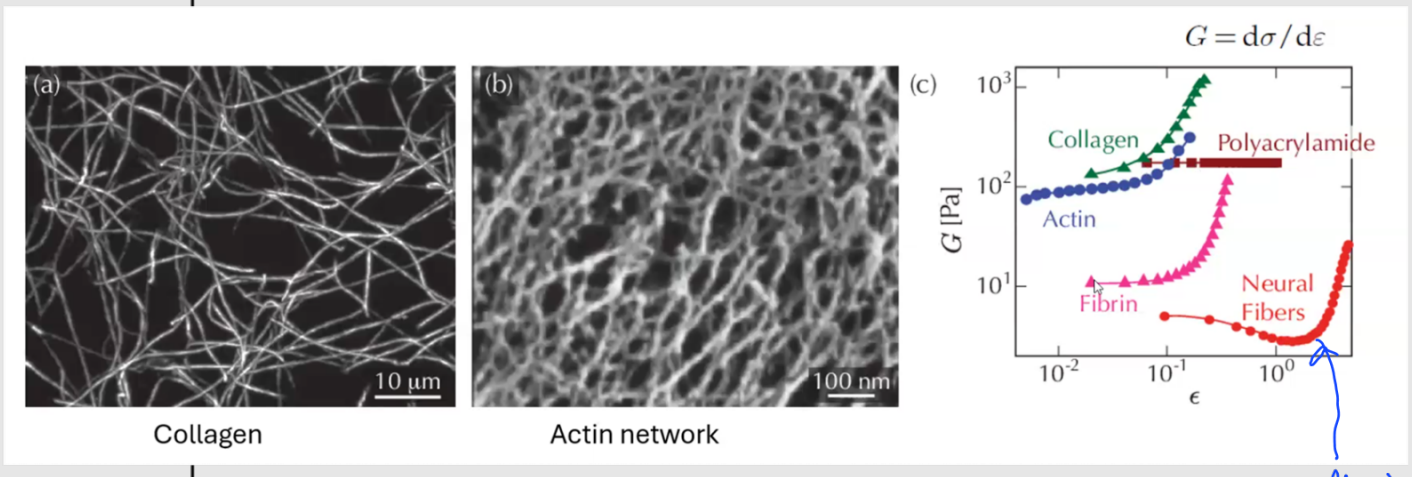



Diblock copolymers (mesophases)

# Response of Biopolymer Networks

- cross-link length $l_{crlk} \lesssim l_p$,
unlike gels with $l_{crlk} \gg l_p$

* Stick to cases with permanent cross-links.




Collagen Actin network

softening before stiffening.

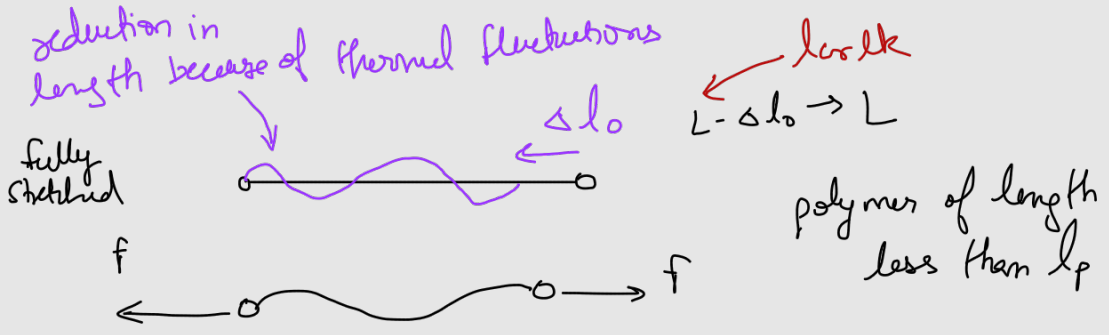
* some questions of interests.

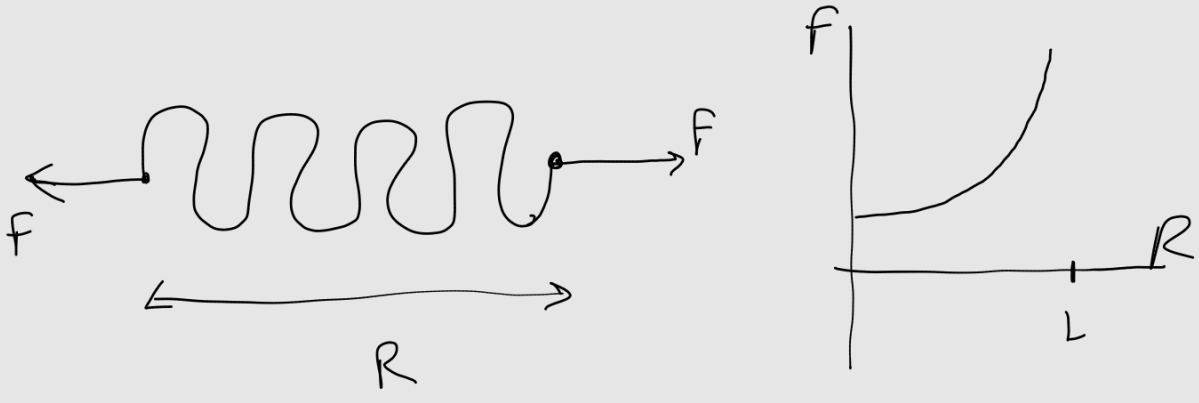
1) Why the stress-strain response is like this?

* when shear is applied, they undergo affine transformations.

a deformation which is a combination of translation, rotation expension and/or stretching

- consider a crosslink polymer:




* to analyze the deformations, we do a fourier mode decomposition of the shape (similar to what was done in WLC model)

## Stretching a clamped fluctuating rod

Similar to worm-like chain, fluctuation-induced contraction of clamped rod under force *f*

$$\langle \Delta \ell \rangle_f = k_B T \sum_q \frac{1}{\alpha q^2 + f} \qquad \alpha = k_B T / \ell_p$$

- this sum runs over the wave numbers $q_n$:

$q_n = \frac{n\pi}{\ell_{crlk}}$, $n = 1, 2, \ldots$

$$\langle \Delta \ell \rangle_0 = k_B T \sum_{q_n} \frac{1}{\alpha q_n^2} = \frac{k_B T\, \ell_{crlk}^2}{\alpha \pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\ell_{crlk}^2}{6\ell_p}$$

The "slack" of the filament

- for small forces $f$, $n=1$ term dominates (i.e. fluctuations by the lowest order bending mode dominates)

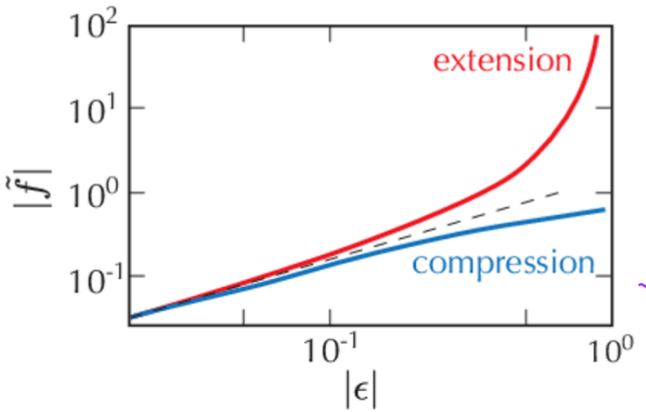
Defining $\delta\ell(f) = \langle \Delta \ell \rangle_0 - \langle \Delta \ell \rangle_f$ ← extension

$$\epsilon = \frac{\delta \ell}{\langle \Delta \ell \rangle_0} = 1 - 3\frac{\pi\sqrt{\tilde{f}}\coth\left(\pi\sqrt{\tilde{f}}\right) - 1}{\pi^2 \tilde{f}} \qquad \tilde{f} = \frac{f \ell_{crlk}^2}{\alpha \pi^2} = \frac{f}{f_c}$$

↑ Strain of the crosslinker.

$$f_c = \frac{\alpha \pi^2}{\ell_{crlk}^2}$$ buckling force

- this motivates defining a reference zero-force contraction due to fluctuations




For small strains, $\delta\ell = \frac{\ell_{crlk}^4}{90\ell_p\alpha} f$ (stiffness weakens with increasing T!)

(since zero-force contraction increases)

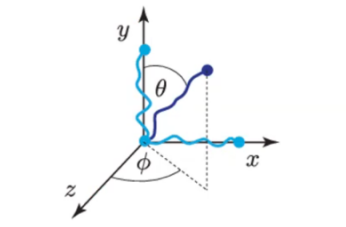
b/c as we increase the temp. we get more slack (prev. pepe polymer diagram), so it's easier to deform.

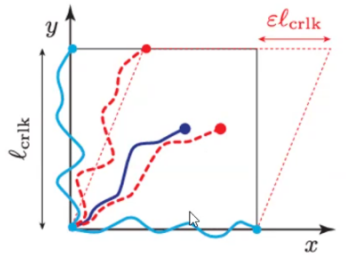
graph of extension,
→ soft at low strains
→ increases (for extension) non linearly at high strains.

also, compression requires low force compared to extension which makes sense.

→ That was about one-crosslinker. Now we move on to applying those results to a biopolymer network ←

## Stress-strain response of a network (affine deformation)




$\varepsilon = \partial u_x / \partial y$

* non linear when $\varepsilon \ell_{crlk} \gtrsim \langle l_0 \rangle$

$$\varepsilon \gtrsim \varepsilon_c \equiv \frac{\langle \Delta l \rangle_0}{l_{crlk}} = \frac{l_{crlk}}{6 l_p}$$

Linear regime:

$$\sigma = \tilde{\rho} \frac{6 \ell_p \alpha}{\ell_{crlk}^3} \varepsilon$$

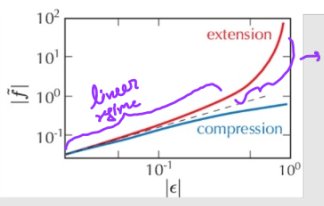
density

$$G_0 = 6 \rho \ell_p \alpha / \ell_{crlk}^3$$

modulus.

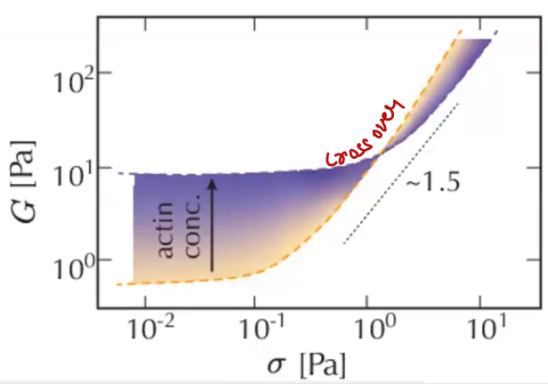
Nonlinear regime:

$$G = \frac{d\sigma}{d\varepsilon} \sim \frac{df}{d\ell} \sim \left(\frac{1}{\Delta \ell}\right)^3 \sim f^{3/2} \sim \sigma^{3/2}$$

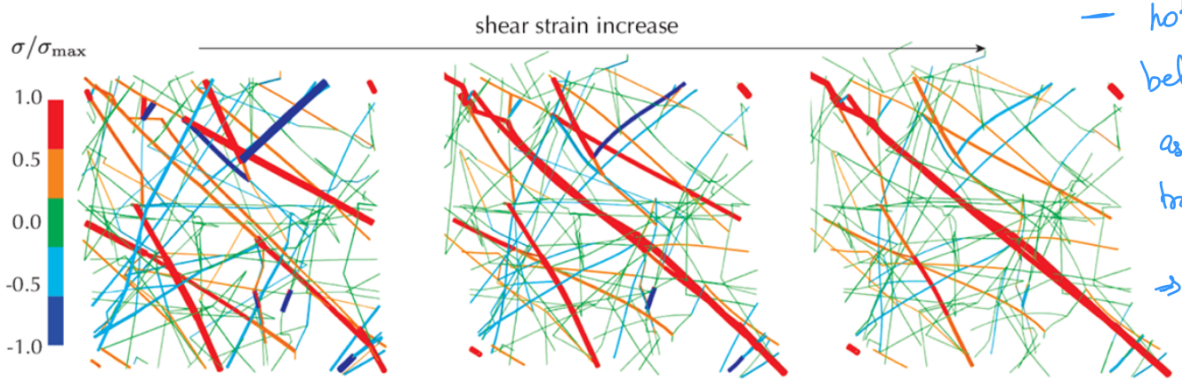



→ non linear regime.

Cross-linked actin network experiments (Gardel et al. 2004)



## Beyond affine approximation

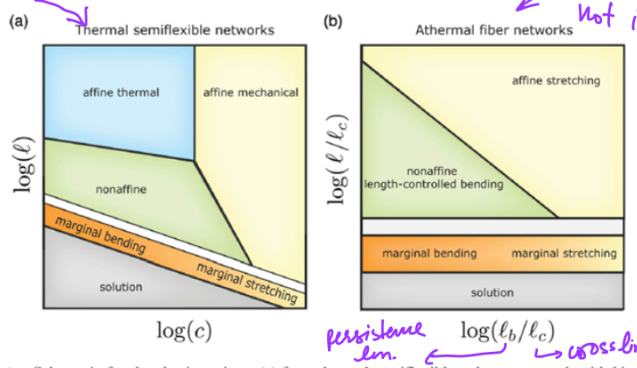



- not a very homogenous behaviour (as opposed to assumptions in affine transformations), i.e. non affine
  - ⇒ but stress stiffening behavior observed is very similar to affine (an open question??)

Simulations of fibers that can bend and stretch show non-affine behavior (Zagar et al. 2011). Gives similar straight stiffening behavior to affine model
Math of non-affine cases are more involved (and in some ways remains areas of research)

slack is important

slack is not important




persistence len. ← $\log(\ell_b/\ell_c)$ → crosslink dist.

FIG. 21 (color online). Schematic for the elastic regimes (a) for a thermal semiflexible polymer network with binary cross-links as a function of two important control parameters: filament length $\ell$ and polymer concentration $c$, and (b) for an athermal fiber network in 3D with binary cross-links as a function of $\ell/\ell_c$ and $\ell_b/\ell_c$. Here $\ell_c$ is the distance between cross-links measured along a filament, and $\ell_b^2$ is set by the ratio between the bending and stretching rigidity of a fiber.

Connectivity of a network as a parameter.

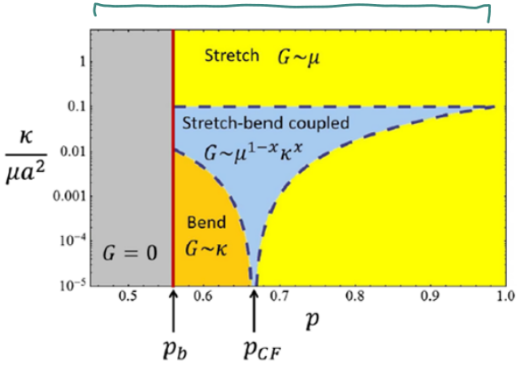


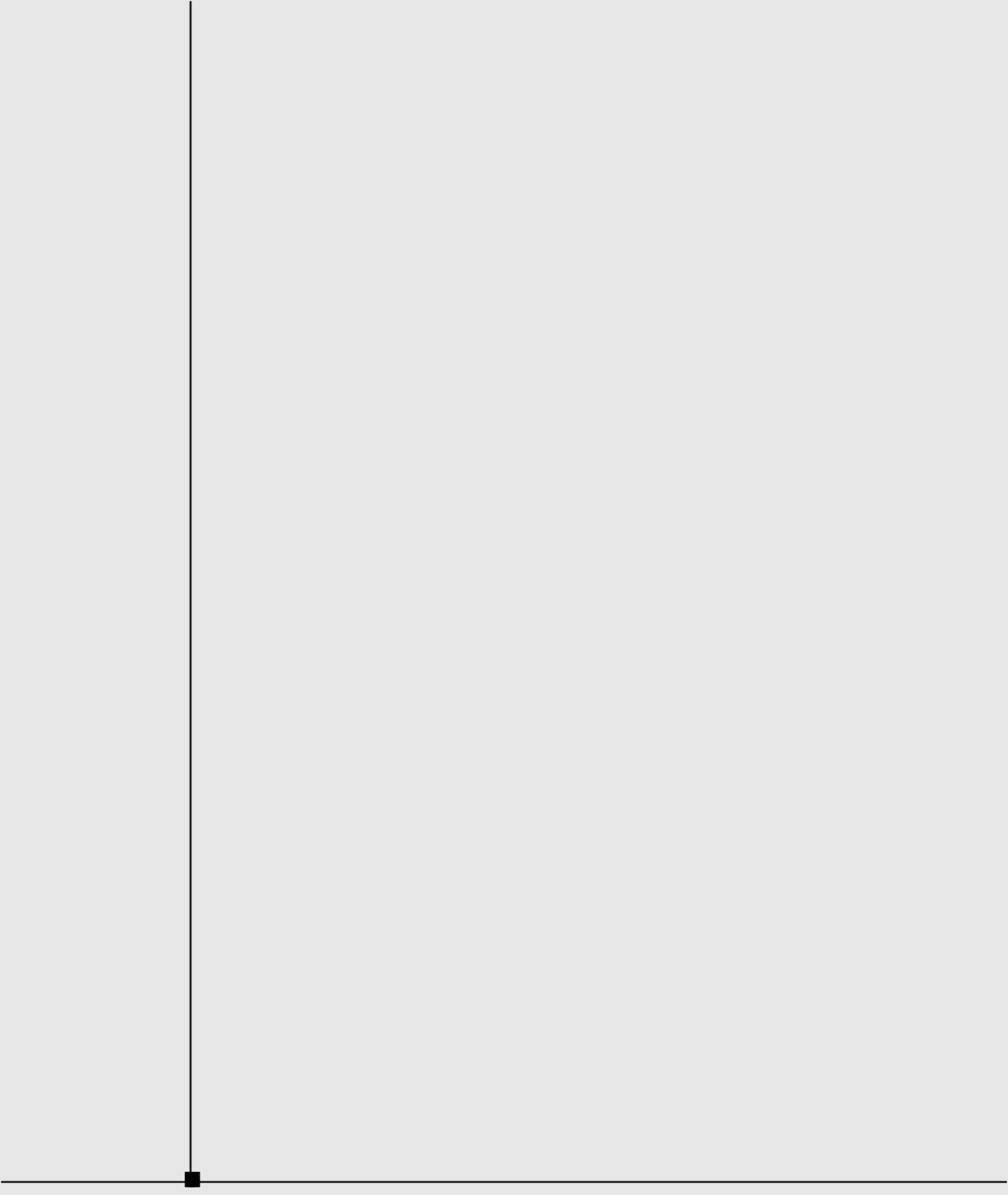

FIG. 24 (color online). Phase diagram for a fibrous network on a diluted triangular lattice. Above the rigidity percolation point $p_b$ there are three distinct mechanical regimes: a stretching-dominated regime with $G\sim\mu$, a bending-dominated regime with $G\sim\kappa$, and a regime in which bend and stretch modes couple with $G\sim\mu^{1-x}\kappa^x$. Here $x$ is related to the critical exponents $x=f_{CF}/\phi$. The mechanical regimes are controlled by the isostatic point $p_{CF}$, which acts as a zero-temperature critical point. Adapted from Broedersz *et al.*, 2011, and Mao, Stenull, and Lubensky, 2013a.

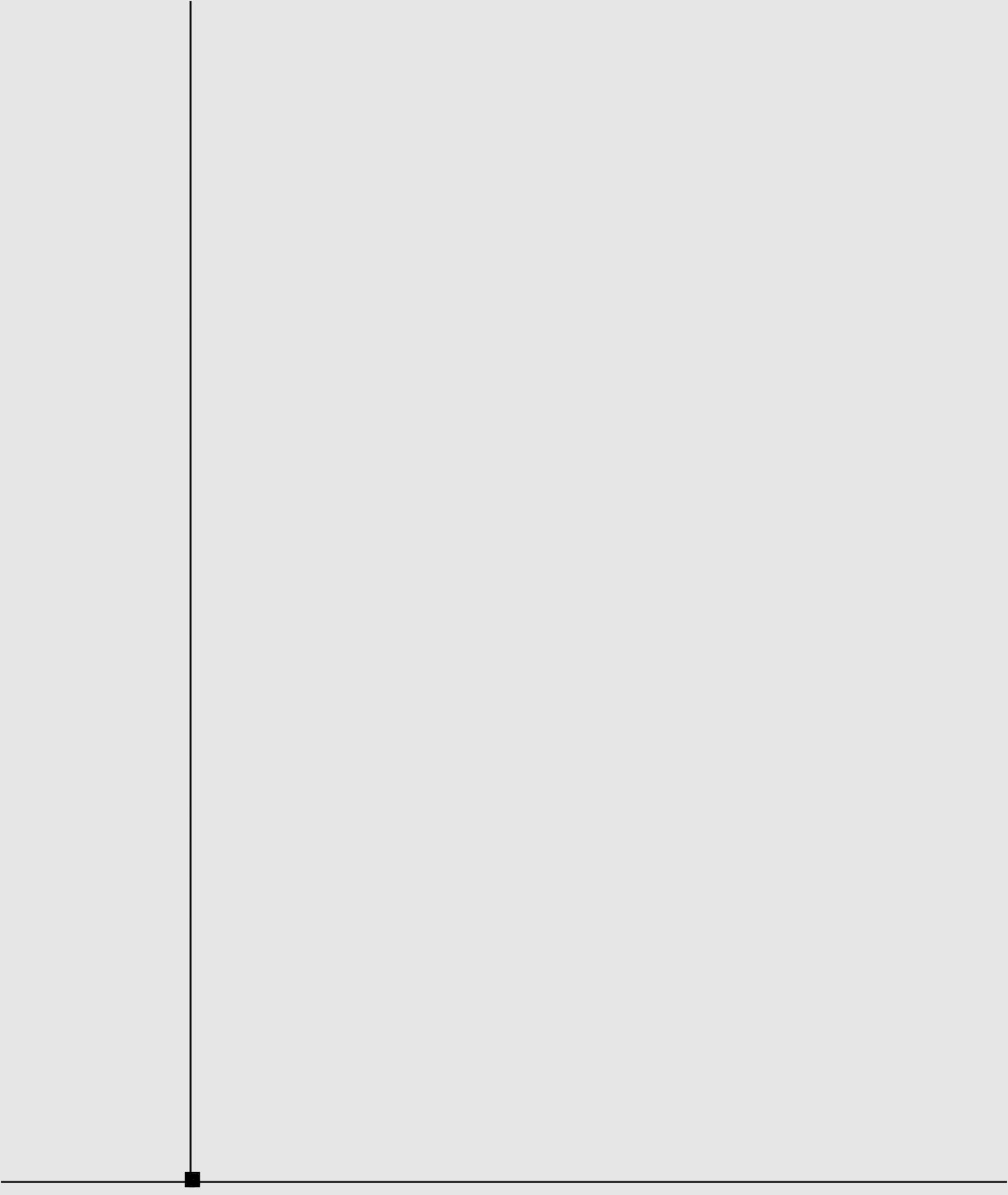
Broedersz and MacKintosh Rev Mod Phys 2014

- a threshold called percolation threshold, above which the network becomes fully connected.
  - ↳ similar to critical point
    - ↳ theoretical frameworks have been proposed to understand the elastic response behaviour by this connectivity parameter.

→ now, we'll look at the results of some simulations without thermal fluctuations.

* the experimental results on previous page (very the slack of the crosslinker), may have been somewhat accidental.





# Reptation and Viscosity of Polymer melts.