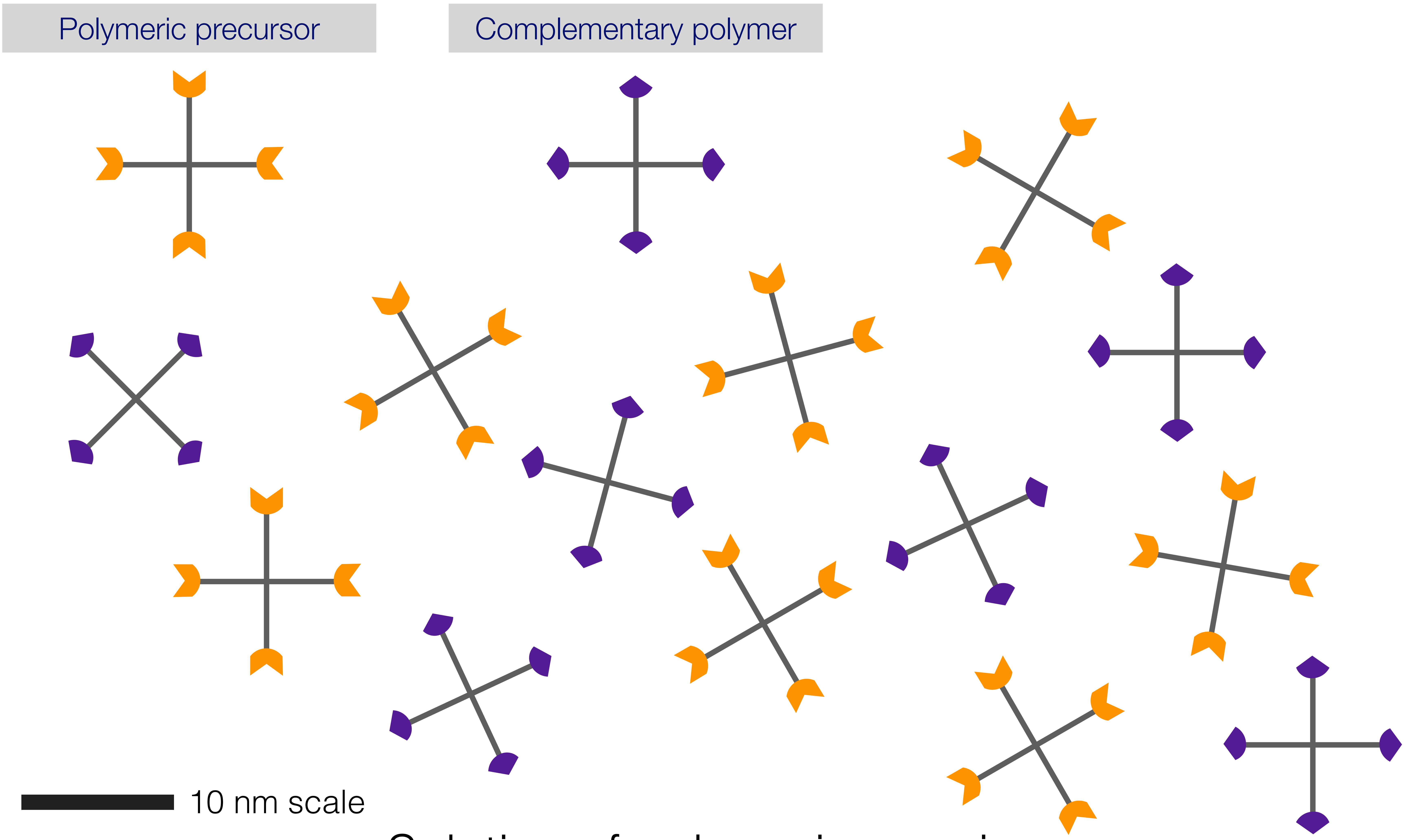
ETH zürich

Macromolecular Engineering: Networks and Gels

Lecture 12: Beyond affine rubber elasticity

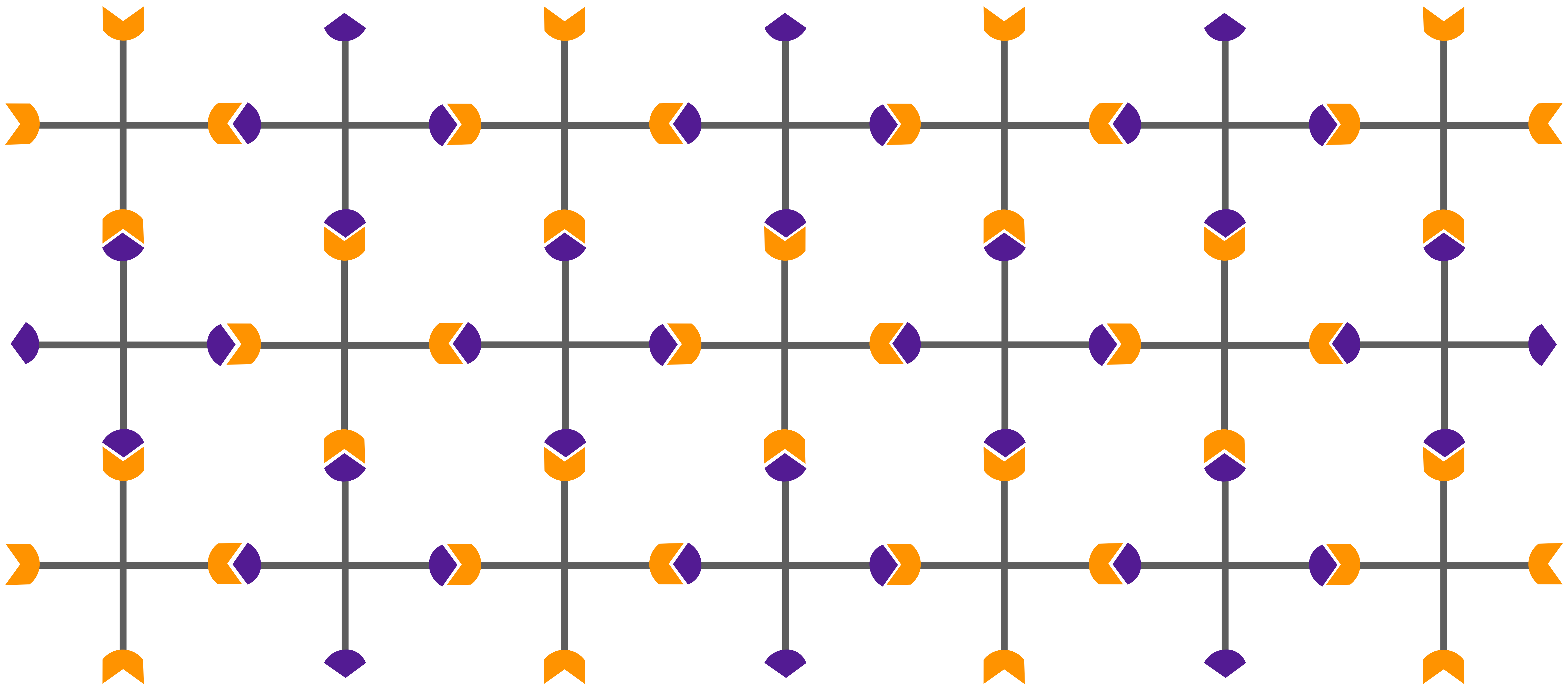
Prof. Dr. Mark W. Tibbitt, 31. March 2022

Macromolecular engineering of networks and gels



Solution of polymeric species

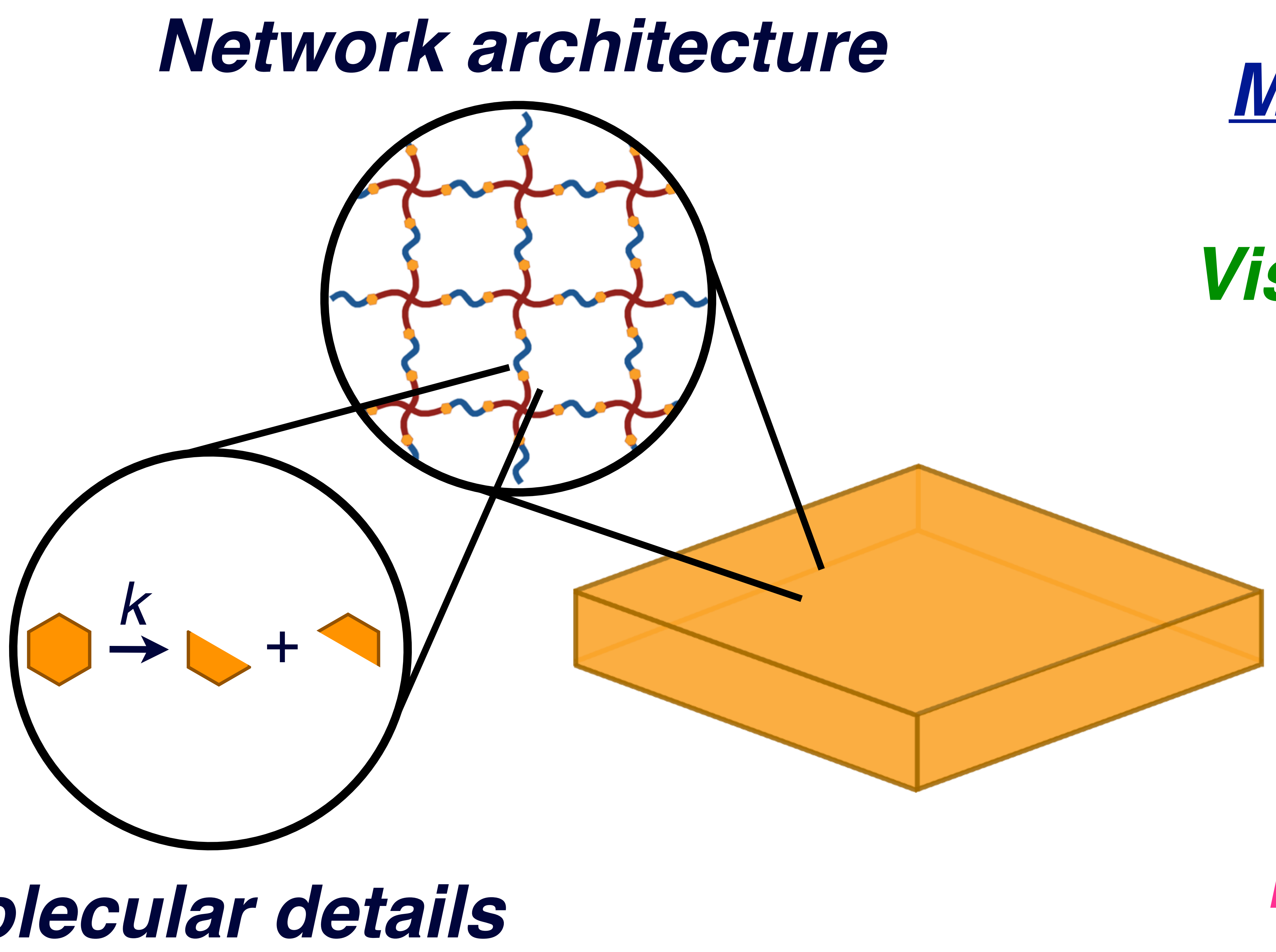
Polymer network or gel



10 nm scale

Viscoelastic insoluble network or gel

Macroscale properties are controlled by molecular details



Macroscale Properties

Viscoelasticity

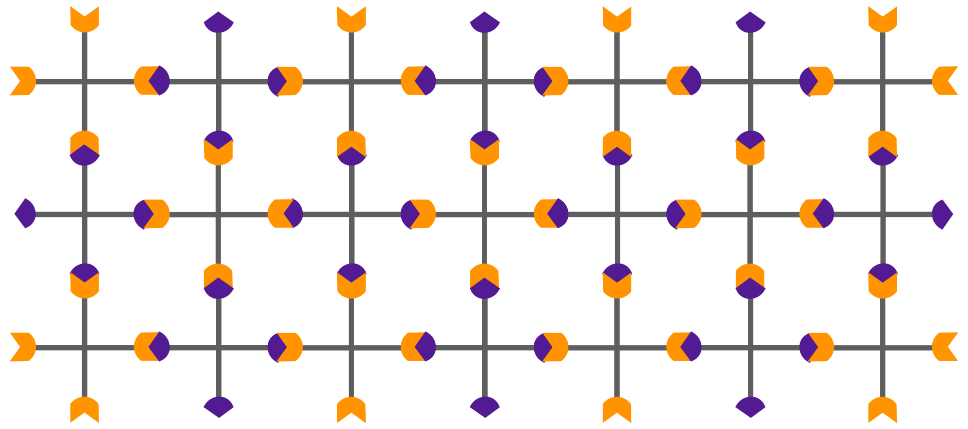
Diffusivity

Surface chemistry

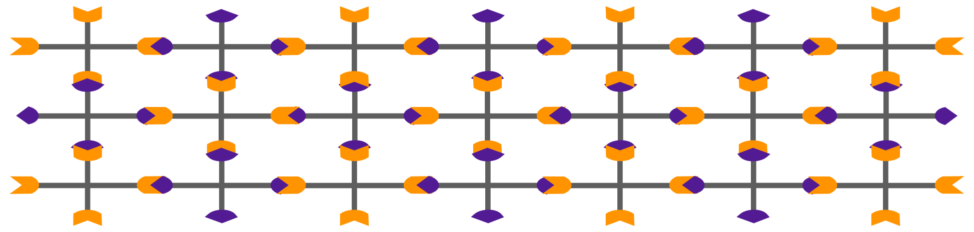
Swelling

Degradation

Macromolecular details inform material properties and provide a tunable handle in their design.



Consider the thermodynamics of the network under deformation

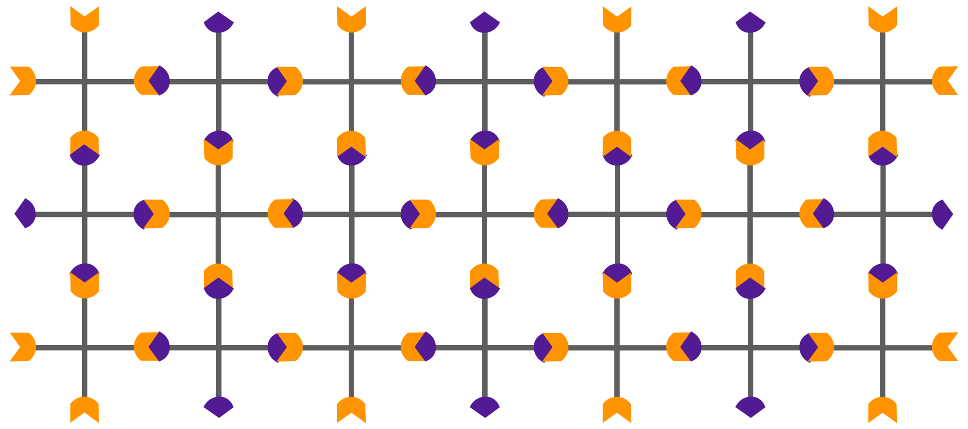


Affine network model - each polymer chain deforms in the same manner that the whole network deforms

Other assumptions

- Gaussian chains
- constant volume
- flexible chains (T > Tg)
- no crystallization at large strain
- energetic component of the free energy = 0

Entropy dominates again!!



$$\sigma_{eng} \equiv \frac{\sigma_{true}}{\lambda} \equiv \frac{nk_BT}{V}\left(\lambda - \frac{1}{\lambda^2}\right)$$

Modulus of the network:

$$G \equiv \nu k_B T$$

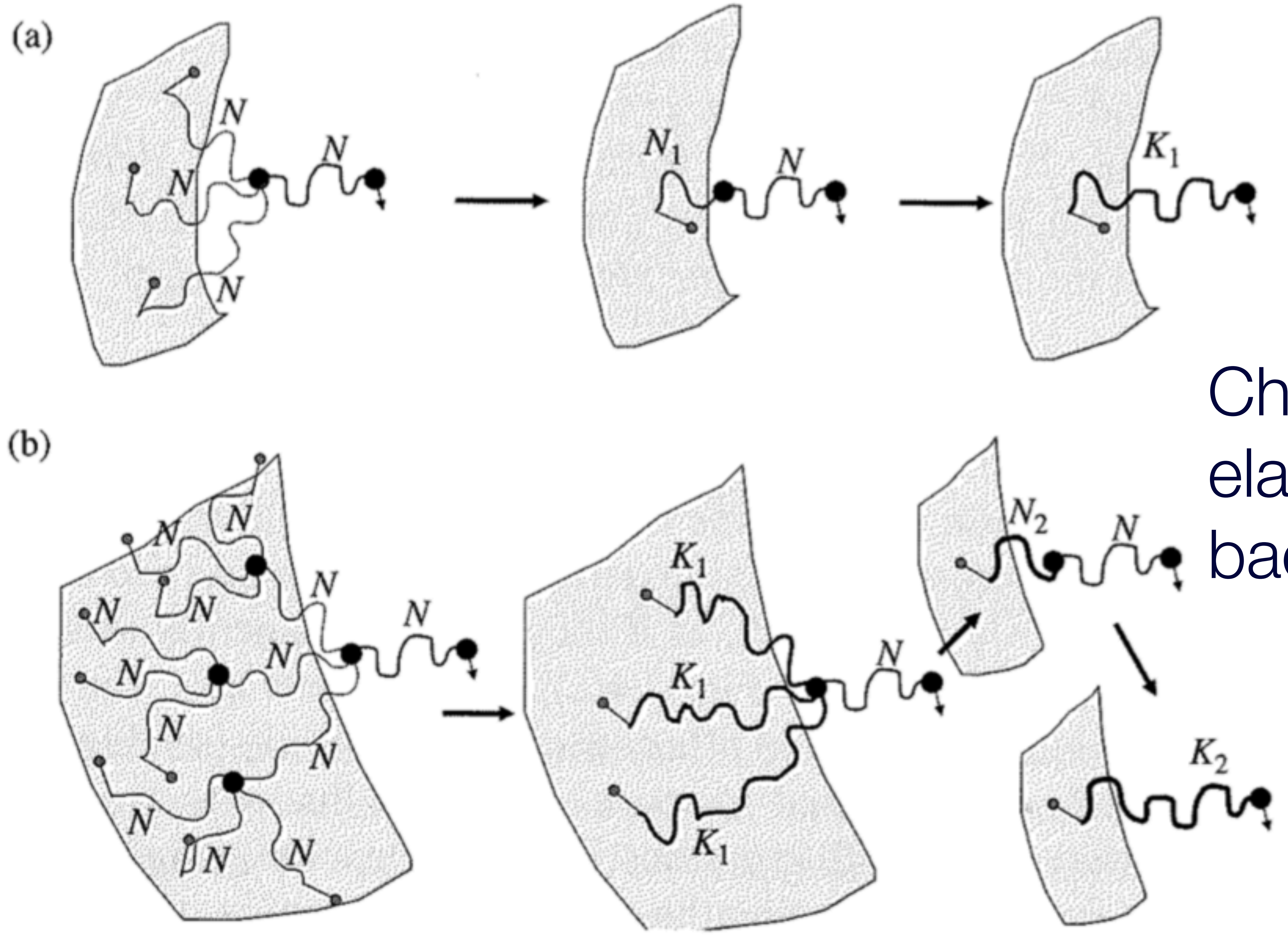
$\nu \equiv$ density of network strands

$$G \equiv \frac{\rho RT}{M_c} = \frac{\rho \mathcal{N}_{av} k_B T}{M_c}$$

$M_c \equiv$ number average molecular weight of the network strand

Modulus scales with temperature and is inverse with molecular weight between crosslinks.

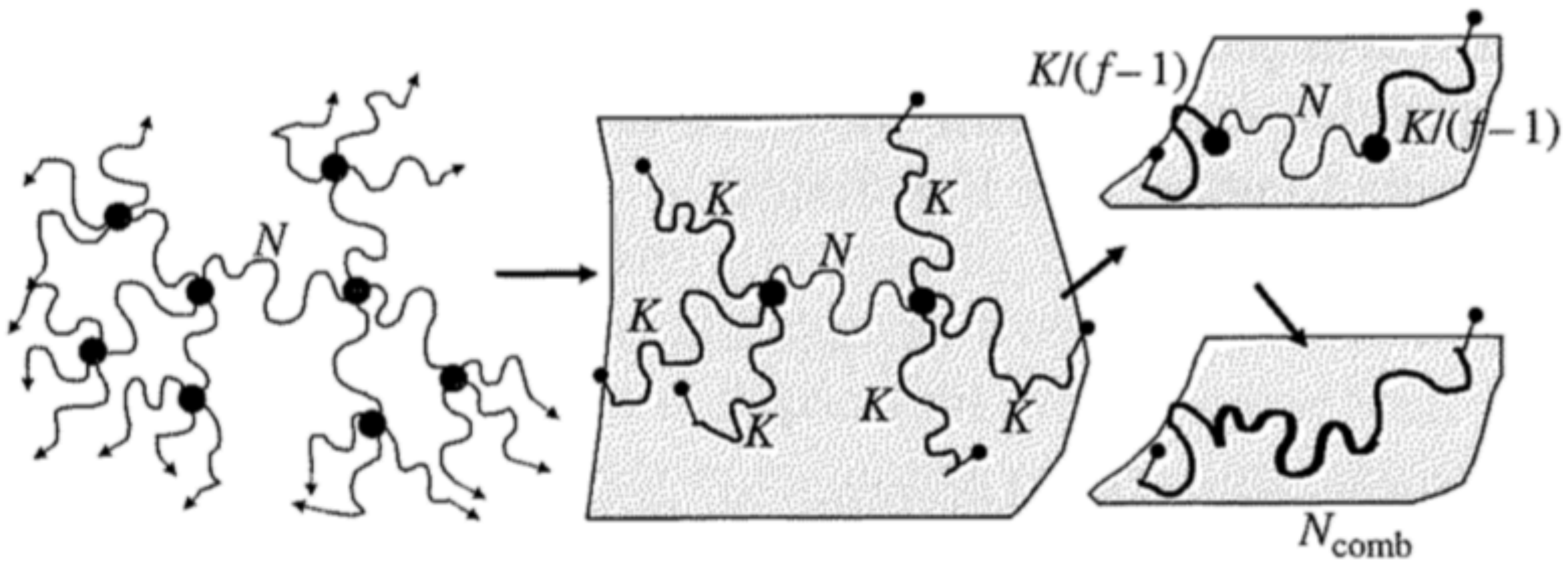
Consider that the junction points in the network can fluctuate but the mean locations are affine. In addition, these fluctuations are Gaussian and independent of the strain.



Chains are connected to an elastic, non-fluctuating background

Polymer Physics Rubinstein and Colby

Phantom network



$$N_{comb} = N + 2\frac{N}{f-2} = \frac{f}{f-2}N$$

$$G = \nu k_B T \frac{f-2}{f} = \frac{\rho RT}{M_c}\left(1 - \frac{2}{f}\right)$$

$$G = k_B T(\nu - \mu)$$

$$\mu \equiv \frac{2\nu}{f}$$ density of crosslinks

Decrease in expected modulus as compared to affine network model

Polymer Physics Rubinstein and Colby

Real Elastic Network Theory (RENT)

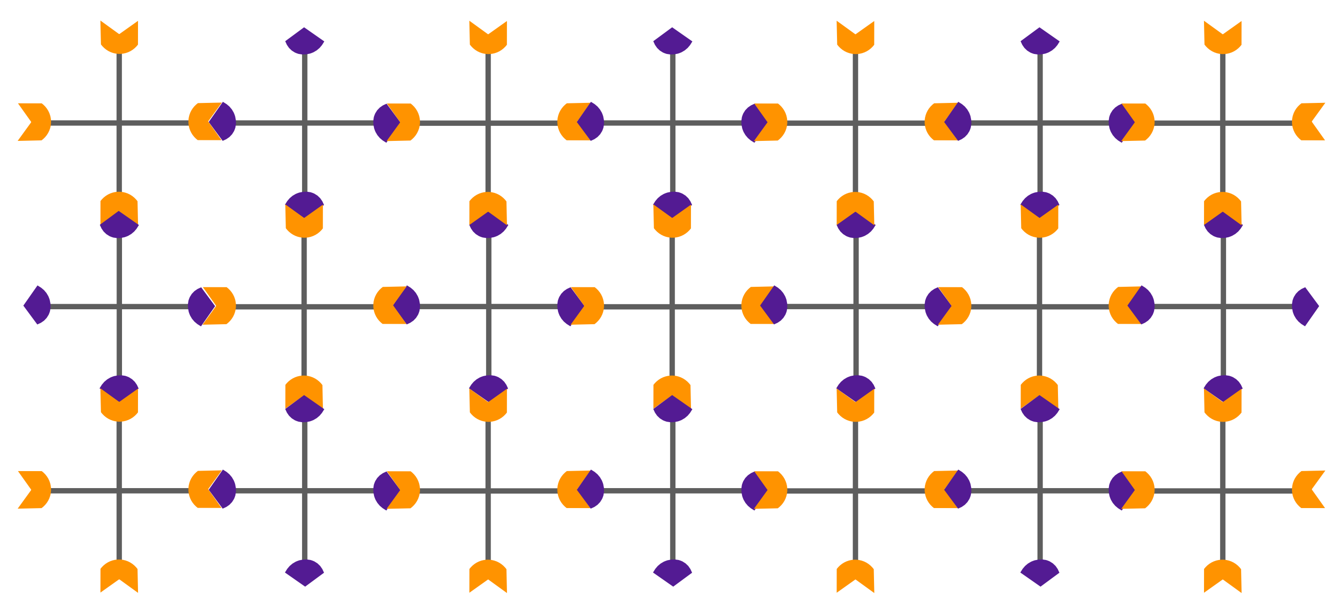
POLYMER SCIENCE

Quantifying the impact of molecular defects on polymer network elasticity

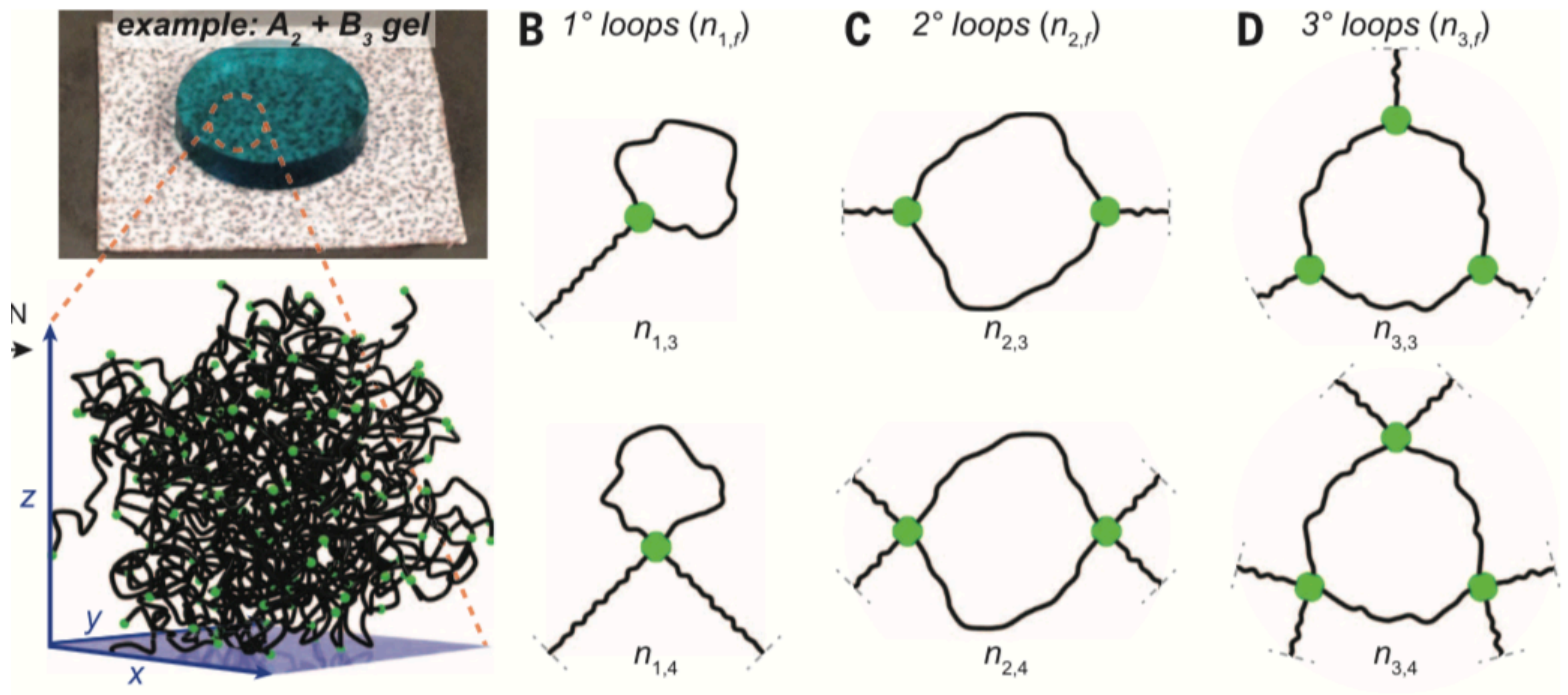
Mingjiang Zhong,[1,2]* Rui Wang,[2]* Ken Kawamoto,[1]* Bradley D. Olsen,[2]† Jeremiah A. Johnson[1]†

Elasticity, one of the most important properties of a soft material, is difficult to quantify in polymer networks because of the presence of topological molecular defects in these materials. Furthermore, the impact of these defects on bulk elasticity is unknown. We used rheology, disassembly spectrometry, and simulations to measure the shear elastic modulus and count the numbers of topological "loop" defects of various order in a series of polymer hydrogels, and then used these data to evaluate the classical phantom and affine network theories of elasticity. The results led to a real elastic network theory (RENT) that describes how loop defects affect bulk elasticity. Given knowledge of the loop fractions, RENT provides predictions of the shear elastic modulus that are consistent with experimental observations.

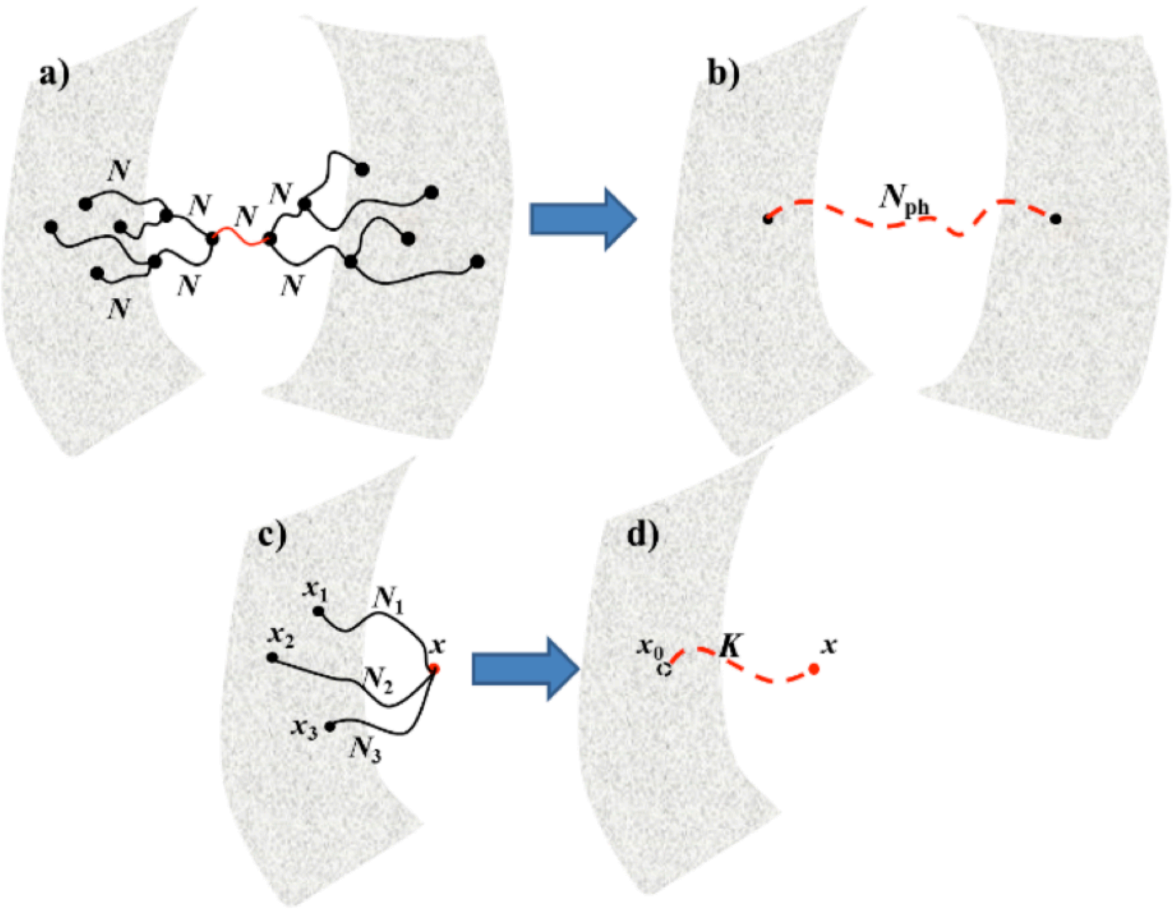
In reality, many loops can be present in the network. Should account for these also!

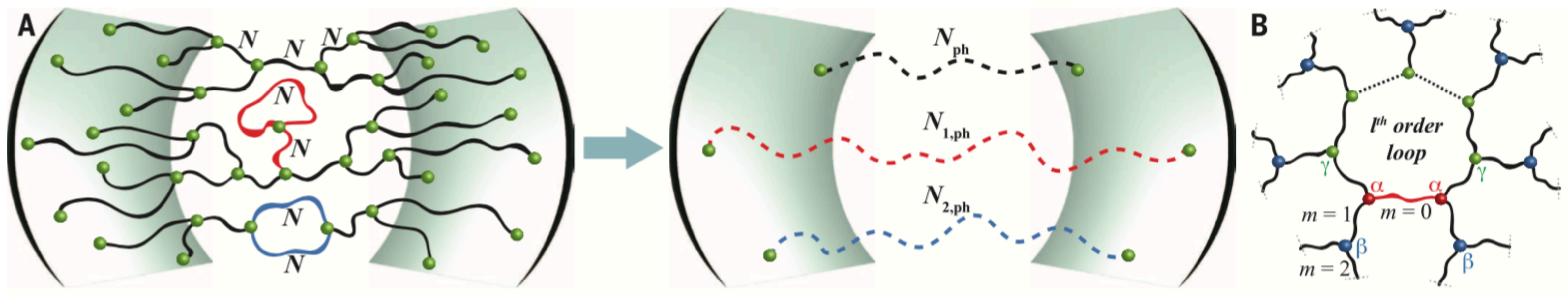


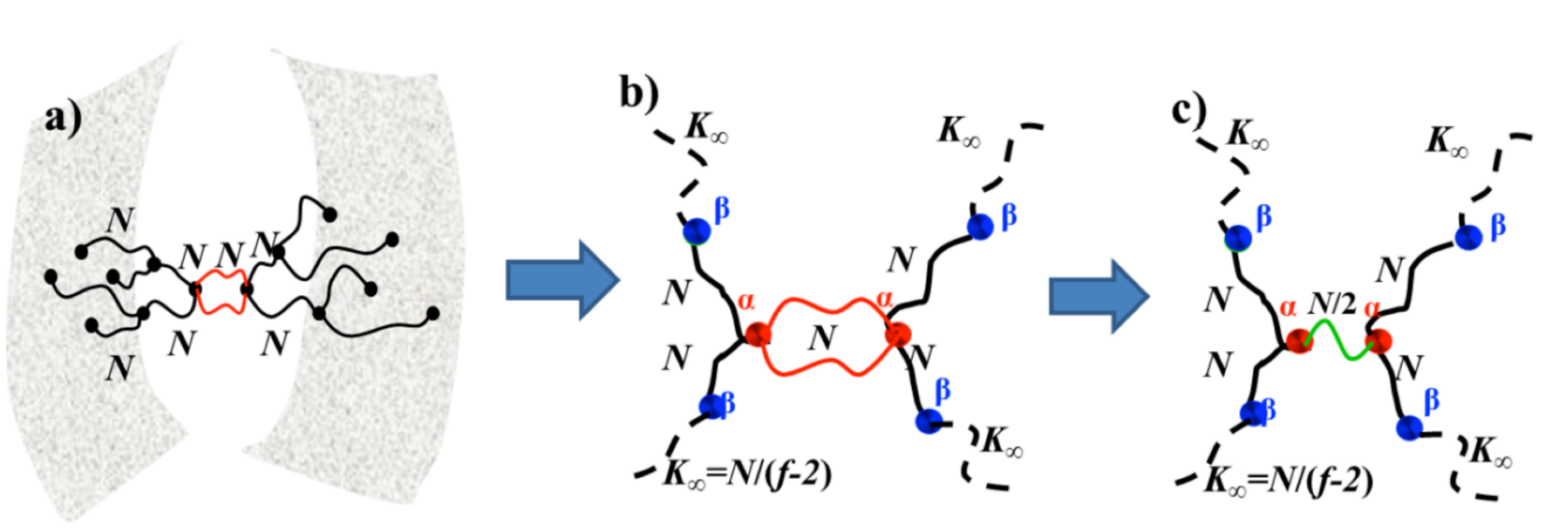
Networks aren't always ideal

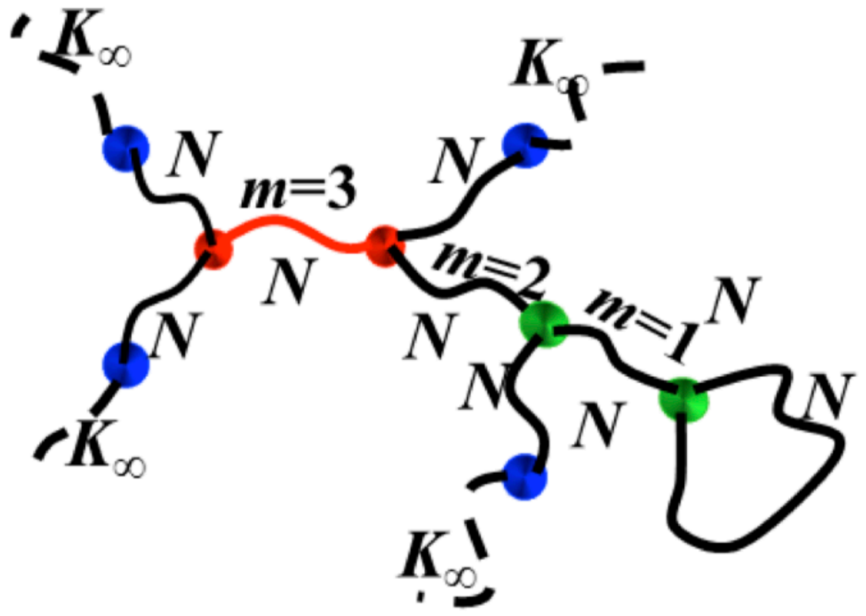


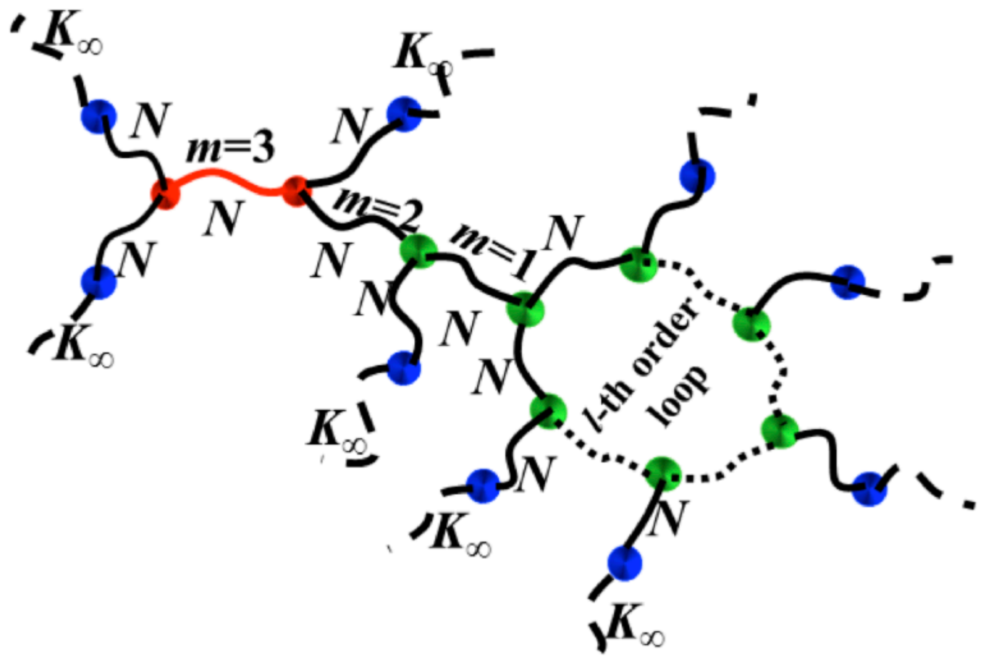
Zhong et al. *Science* 2016, **353**, 1264–1268











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$$\frac{G'}{\nu_0 kT} = \frac{f-2}{f}\left(1 - A_f n_{1,f} - B_f n_{2,f} - \sum_{l=3}^{\infty} C_{l,f} n_{l,f}\right) \quad (8)$$

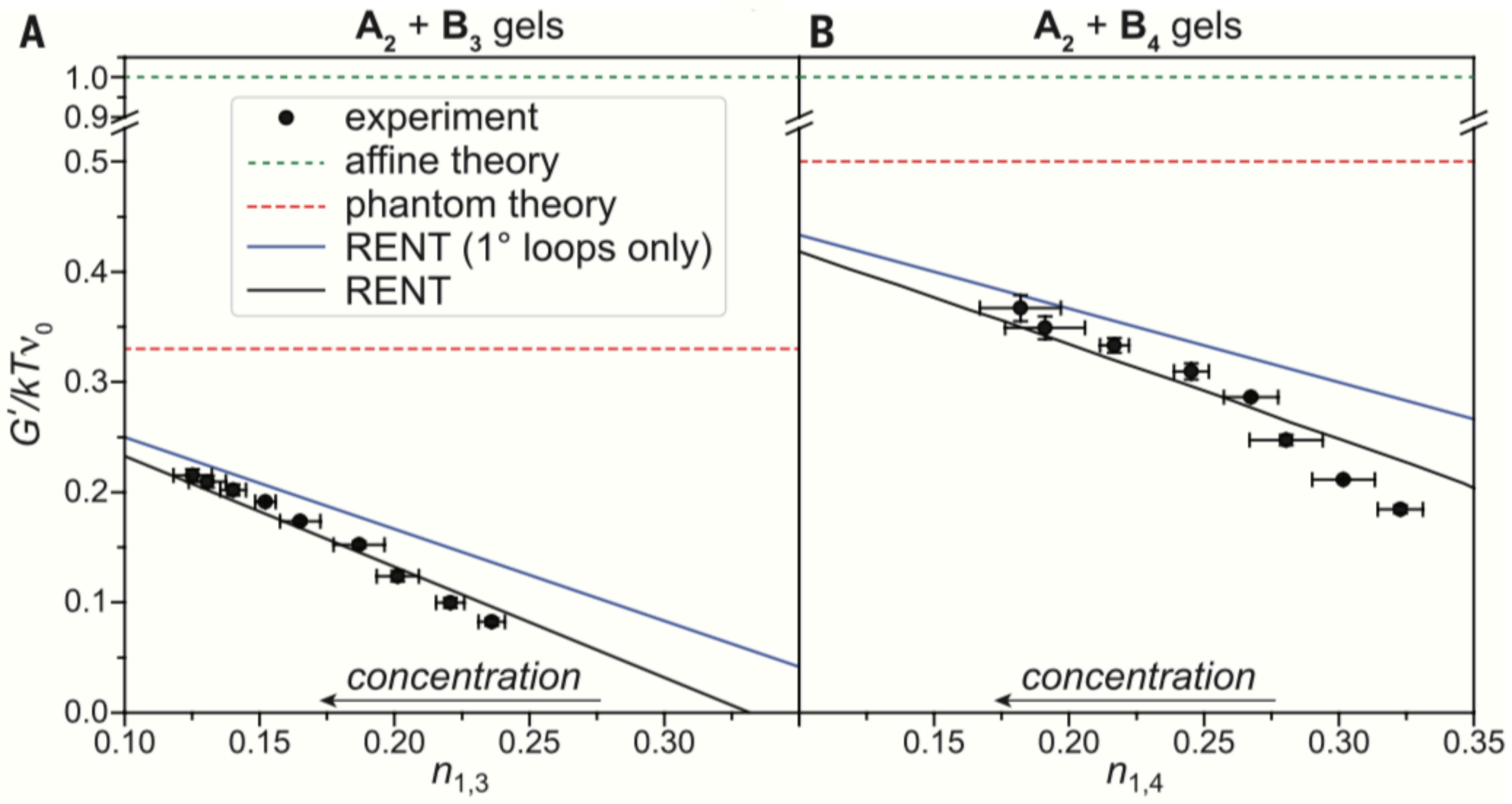
with

$$A_f = \begin{cases} 5/2 & \text{for } f = 3 \\ 4/3 & \text{for } f = 4 \\ 2/(f-2) & \text{for } f \geq 5 \end{cases} \quad (9)$$

$$B_f = \frac{4(f-1)}{f^2(f-2)} \quad (10)$$

and

$$C_{l,f} = \frac{4}{f}\left[\frac{1}{(f-1)^{2l-2}+1} + \frac{1}{(f-1)^{2l-1}-1}\right] \quad (11)$$



A further decrease in expected modulus from the phantom network model because of network defects!

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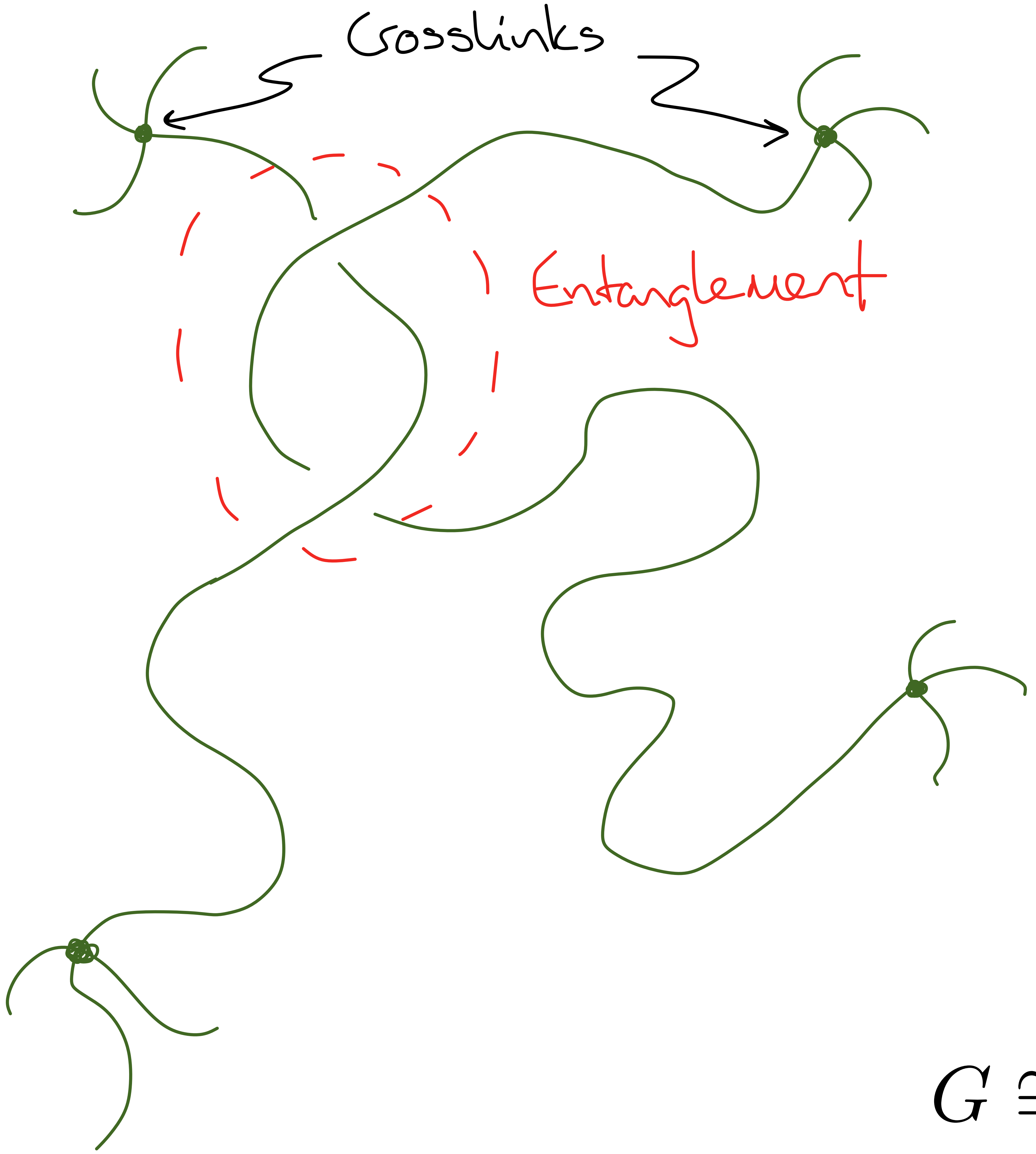

Consider a ‘second’ network that is cross-linked by entanglements

$$G_e = \frac{\rho R T}{M_e}$$

$M_e \equiv$ number average molecular weight between entanglements

Total modulus for the system that is the sum of the contributions from cross-links and entanglements

$$G \cong G_c + G_e \approx \rho R T \left(\frac{1}{M_c} + \frac{1}{M_e} \right)$$

Rubber Elasticity - summary

The mechanical properties of networks and gels are imparted mostly by changes in entropy of network strands upon deformation.

The modulus G of a network or gel is proportional to the number density of elastically active network strands with each strand contributing kT.

When calculating modulus it is important to take into account network topology such as loops and entanglements.