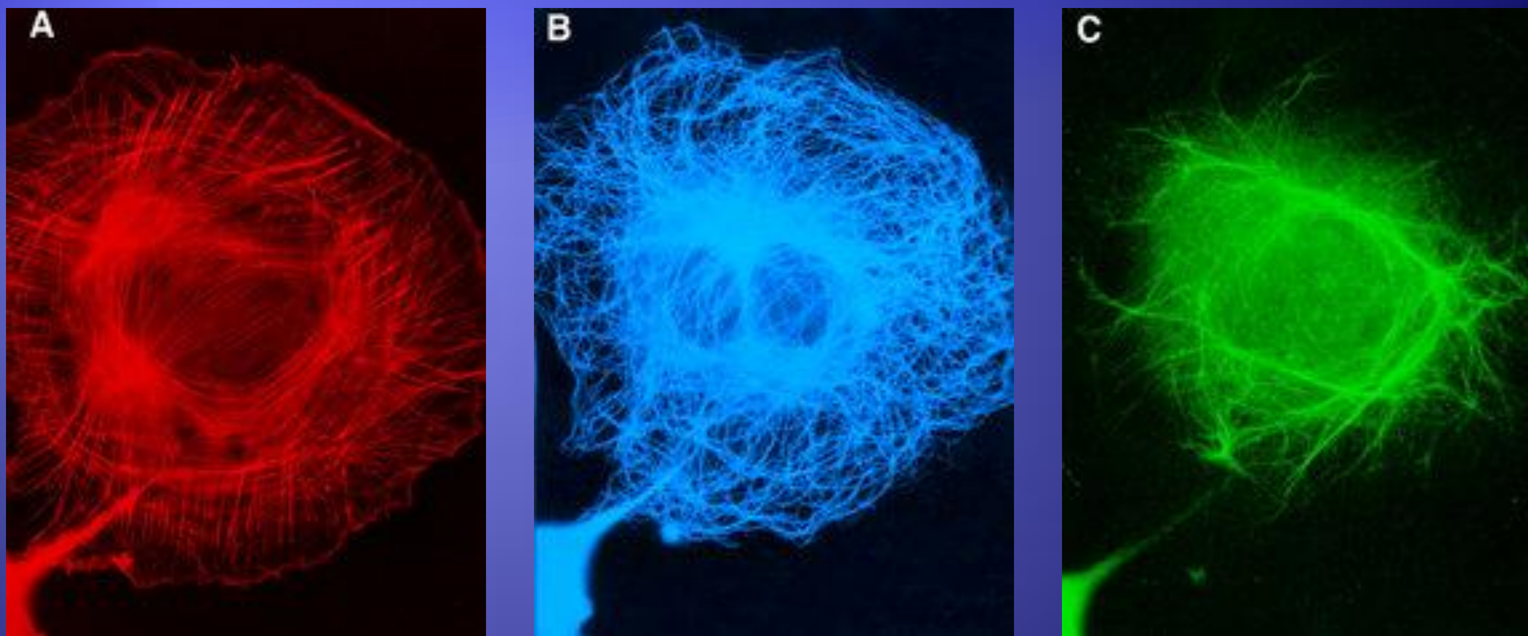
Session 16

# SEMIFLEXIBLE POLYMER NETWORKS

# Recall: Cytoskeleton

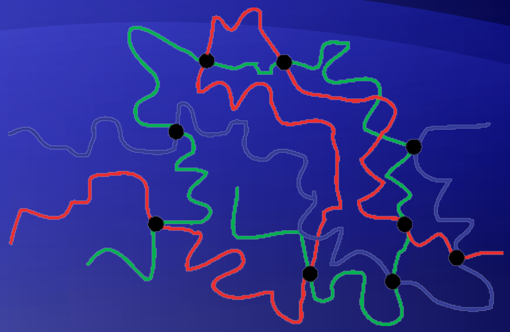
- Three fundamental cytoskeletal filaments




Actin | Microtubules (MT) | Intermediate Filaments (IF)

# Rubber (Elastomer)

- Random coiling of polymer filaments
- Cross-linking between filaments (black dots)
- Entropic Spring
  - Stretching force cause order in filaments
  - Reduces entropy
  - Generates of heat



# Thermodynamics of Rubber

- Consider the 1st Law of Thermodynamics

$$\Delta U = Q + W$$

  - $\Delta U$: change in internal energy (strain energy)
  - Q: heat *added to* system
  - W: work done *on* system

- For reversible system, heat added is equal to temperature of system times change in entropy

$$Q = T\,\Delta U$$

# Thermodynamics of Rubber

- Consider the 1st Law of Thermodynamics

$$\Delta U = Q + W$$

$$Q = T\,\Delta S$$

- Work done on system is equal to applied force times change in length of system

$$W = F\,\Delta L$$

# Thermodynamics of Rubber

- Consider the 1st Law of Thermodynamics

$$\Delta U = Q + W$$

$$Q = T\,\Delta S$$

$$W = F\,\Delta L$$

$$\Delta U = T\,\Delta S + F\,\Delta L$$

- Stretching rubber rotates its bonds, does not stretch bonds…

$$0 = T\,\Delta S + F\,\Delta L$$

# Thermodynamics of Rubber

- Rearranging…

$$F\,\Delta L = -\,T\,\Delta S$$

- As rubber extends under force F = 1, e.g. ΔL = 2

$$2 = -\,T\,\Delta S$$

  - RHS must be positive
  - But, temperature cannot be negative (T in Kelvins)
  - Thus, change in entropy must be negative (-ΔS)
  - As a consequence, stretched rubber gives off heat

$$Q = T\,\Delta S$$

$$(-Q) = T\,(-\Delta S)$$

(What if you add heat back in?)

# Simple Case: Entropy of Filaments

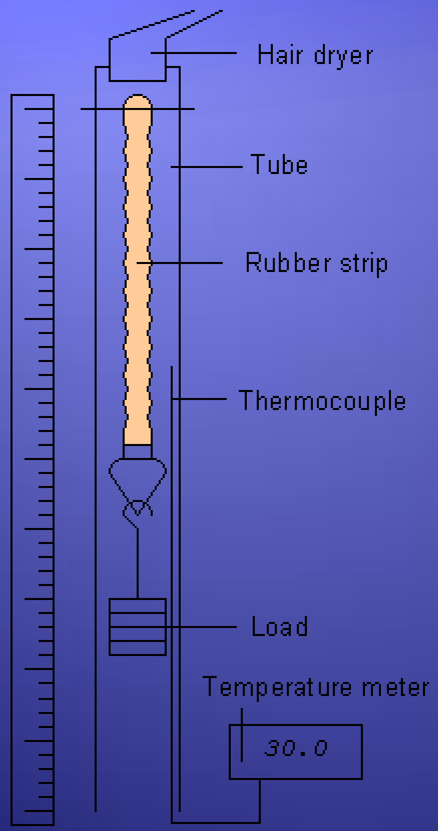
- Consider four-segment polymer

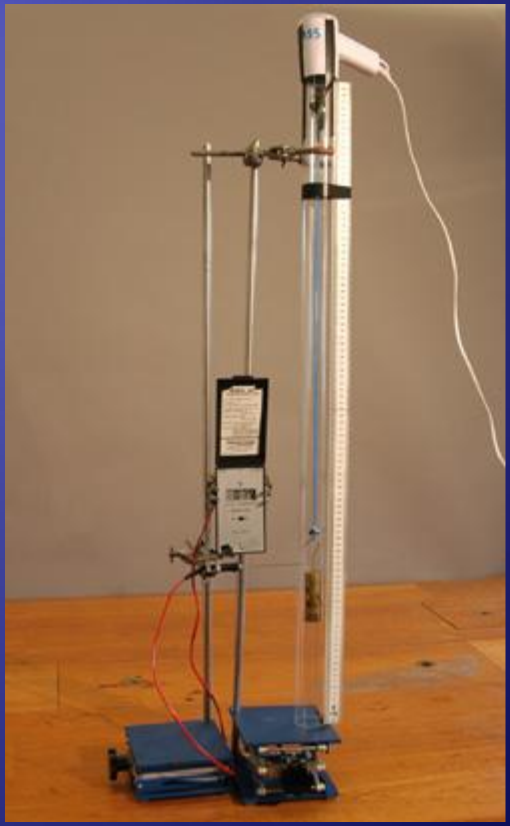
- There are 16 unique configuration states
  - $S \approx \ln(16) = 2.77$
- There is tension applied such that there cannot be zero separation from end-to-end
  - $S \approx \ln(10) = 2.30$


- Therefore, tension reduces entropy

# Fun Experiment

- Entropic stiffness is proportional to temperature

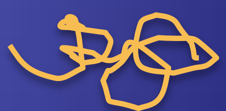


# Persistence Length $l_p$

- Simply, filaments in thermal equilibrium in a liquid solution will appear…
  - Straight over lengths < $l_p$
  - Contorted randomly over lengths > $l_p$

Hi $l_p$



Lo $l_p$

- In vitro solution measurements:
  - DNA: 50 nm
  - F-actin: 17 μm
  - Microtubule: 1 mm

# Persistence Length $l_p$

- Formally,

$$l_p = \frac{\kappa}{kT}$$

where

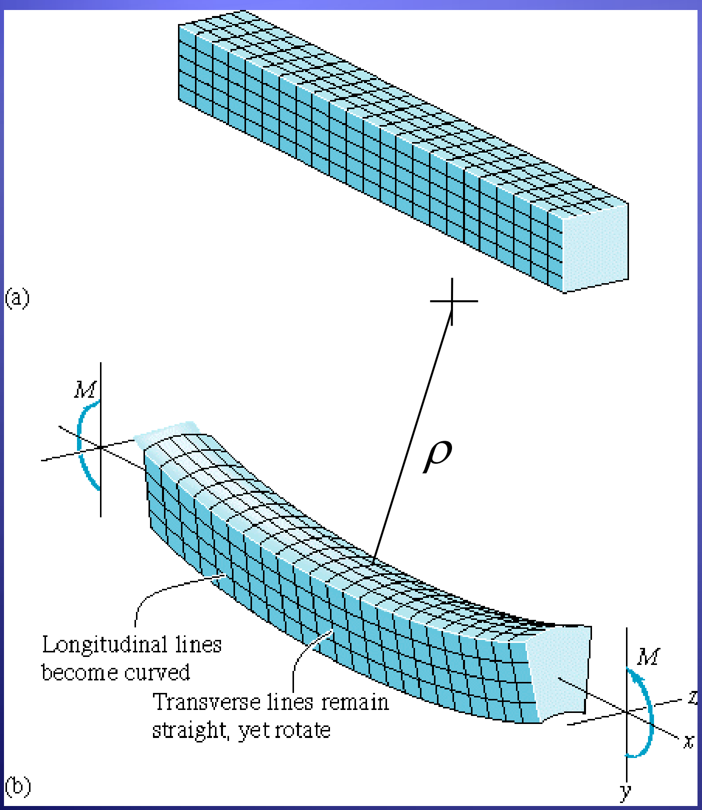
$\kappa = E_Y I$ is bending stiffness

k = 1.38 x $10^{-23}$ J/K is Boltzmann constant

T is temperature in K

# Bending Energy

- Applied forces lead to moment $M$ in rod
- $M$ acts to deforms straight shape to curved shape




- Strain Energy

$$W = \frac{1}{2} F_x \Delta x$$

- Infinitesimal Strain Energy

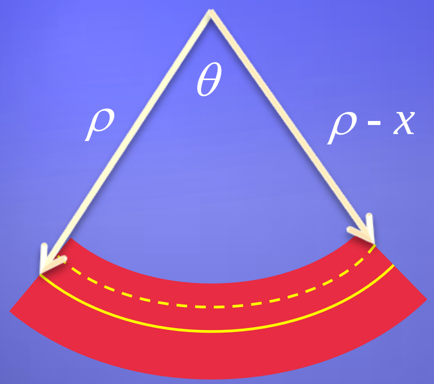
$$U = \frac{W}{V} = \frac{1}{2} \sigma_x \varepsilon_{xx}$$

- By Hooke's Law

$$U = \frac{1}{2} E_Y \varepsilon^2_{xx}$$

# Bending Curvature

- Interior bending lengths




$$L_{NA} = \rho\theta$$ Length along neutral axis

$$L' = (\rho - x)\theta$$ Length along dashed line

- Strain

$$\varepsilon_{xx} = \frac{(L' - L)}{L} = -\frac{x}{\rho}$$

- Thus…

$$U = \frac{1}{2} E_Y \left(\frac{x}{\rho}\right)^2$$

# Bending Energy

- Strain energy per unit length

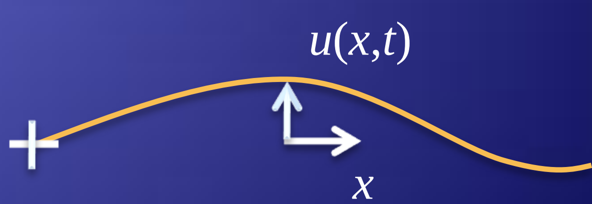
$$
\begin{aligned}
E &= \int_A \frac{1}{2} E_Y \frac{x^2}{\rho^2} dA \\
&= \frac{1}{2} \frac{E_Y}{\rho^2} \int_A x^2 dA \\
&= \frac{1}{2} \frac{E_Y I_y}{\rho^2} \\
&= \frac{\kappa}{2} \frac{1}{\rho^2}
\end{aligned}
$$

# Worm-like Chain Model

- Energy can be described as

$$\boxed{H_{bend} = \frac{\kappa}{2}\int_{l} \frac{1}{\rho^2}\, ds}$$

- Radius of curvature


$$\frac{1}{\rho} = \frac{\partial \vec{t}}{\partial s}$$

$$\frac{1}{\rho} \simeq \frac{\partial^2 u}{\partial x^2}$$

# Worm-like Chain Model

- We can express as

$$H_{bend} = \frac{\kappa}{2}\int_l \left(\frac{\partial \vec{t}}{\partial s}\right)^2 ds$$

- Or

$$H_{bend} = \frac{\kappa}{2}\int_l \left(\frac{\partial^2 u}{\partial x^2}\right)^2 dx$$

# Force – Extension Relationship

- Tension to extend a filament measured by amount of extension along a line

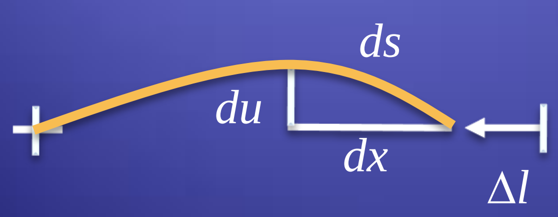

- Extension response dominated by entropy
- At any finite temperature, there is contraction due to thermal fluctuations that makes polymer deviate from straight line

# Force – Extension Behavior

- Semiflexible chain stretched by tension $\tau$
  - Energy of bending $H_{bend}$
  - Energy of contraction against $\tau$

- Derive the "shortening" in the filament:

*Length is unchanged by kT, $\tau$*




$$\begin{aligned}\Delta l &= \int (ds - dx) \\ &= \int \left(\sqrt{dx^2 + du^2} - dx\right) \\ &= \int \left(\left(\sqrt{1 + \left(\tfrac{\partial u}{\partial x}\right)^2}\right) - 1\right) dx \\ &\simeq \tfrac{1}{2} \int (\partial u / \partial x)^2 \, dx\end{aligned}$$

# Deformation Behavior

- Strain energy from stretching

$$H_{stretch} = \frac{1}{2}\int_{l}(\tau \cdot \Delta l)dx = \frac{1}{2}\int_{l}\tau\left(\frac{\partial u}{\partial x}\right)^{2}dx$$

- Thus, total energy

$$\begin{aligned} H &= H_{bend} + H_{stretch} \\ &= \frac{1}{2}\int_{l}\left(\kappa\left(\frac{\partial^{2} u}{\partial x^{2}}\right)^{2} + \tau\left(\frac{\partial u}{\partial x}\right)^{2}\right)dx \end{aligned}$$

- Note, there exists version for transverse motion

# Spring Constants

- It can be shown …
  - Transverse spring constant

$$k_{sp,bend} \simeq \frac{kTl_p}{l^3}$$

  - Longitudinal spring constant

$$k_{sp,stretch} \simeq \frac{kTl_p^2}{l^4} = k_{sp,bend}\frac{l_p}{l}$$

  - For $l < l_p$, longitudinal stiffness is lower than transverse

# Force – Extension Behavior

- It can be shown
  - Considering the balance with thermal energy
  - Adding transverse motion direction, and
  - Utilizing statistical mechanics concepts

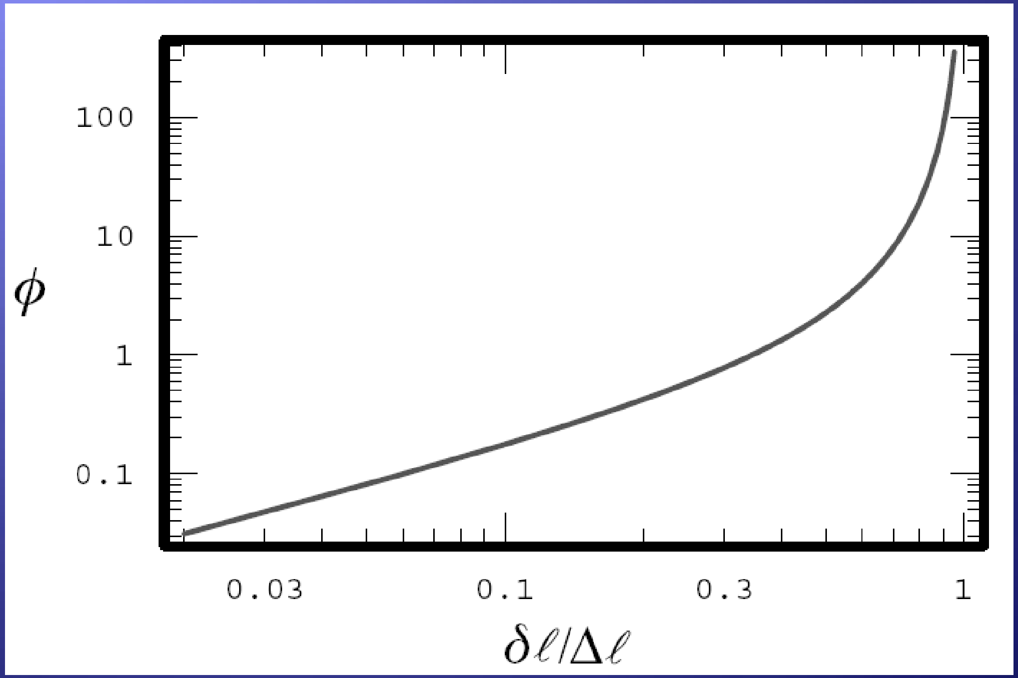
$$\delta l = \frac{kT}{\pi^2}\frac{l^2}{\kappa}\sum_n \frac{\phi}{n^2\left(n^2+\phi\right)}$$

with dimensionless force

$$\phi = \tau l^2 / \kappa\pi^2$$

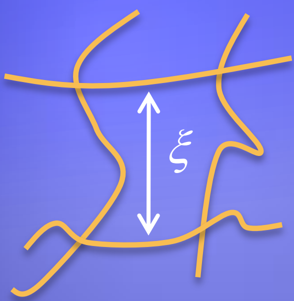
# Force - Extension

- Non-linear behavior
  - Linear at small force
  - Strain stiffening at large forces

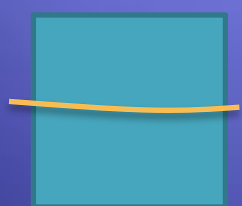


# Polymer Interactions

- Solution of polymers have mesh size dimension $\xi$




  - Typical spacing between filaments
  - Estimated by volume fraction $\psi$
  - For rigid rods (lengths < $l_p$)



$$\psi = \frac{V_{filament}}{V_{mesh}} = \frac{a^2\xi}{\xi^3}$$

  - Accounting for thermal fluctuations

$$\psi = \frac{V_{transverse}}{V_{longitudinal}} = \frac{a^2\delta u}{\frac{1}{3}\pi l\delta u^2} = \frac{a^2}{l\delta u} = \frac{a^2}{l_e\delta u}$$

# Shear Modulus for Solutions

- It can be shown that for entropy only

$$G \sim kT \Big/ \left( \xi^2 l_e \right) \sim \psi^{7/5}$$

  - Temperature dependence
  - Filament density dependence

# Shear Modulus for Solutions

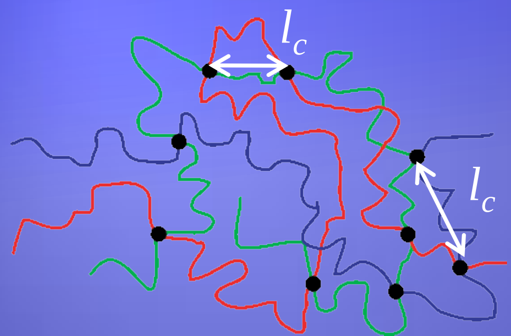
- High frequency testing
  - Filaments not able to relax from high bending modes
  - Increased stiffness from less compliant filaments

$$G(\omega) = \frac{1}{15}\rho\kappa l_p \left(-2i\zeta/\kappa\right)^{3/4}\omega^{3/4} - i\omega\eta$$

$\rho$ is polymer concentration, $\zeta$ is hydrodynamic drag (per unit length) , $\eta$ is viscosity

# Shear Modulus for Networks

- Consider cross-linking distance $l_c$





- Deformation types
  - Affine network models: uniform rotation or stretching
  - Non-affine models: macroscopic strains vary from one region to another

# Shear Modulus for Networks

- Affine, thermal-entropic (AT)

$$G_{NA} \sim \kappa / \xi^4 \sim \psi^2$$

  - Modulus depends strongly on x-linking

- Non-affine (NA)
  - Low poly conc, high x-linking (low $l_c$)

$$G_{AT} \sim \kappa l_p / \xi^2 l_c^2$$

- Affine, mechanical (AM)
  - Filament segments (small $l_c$) behave as rigid rods with modulus $\mu$

$$G_{AM} \sim \mu / \xi^2 \sim \psi$$