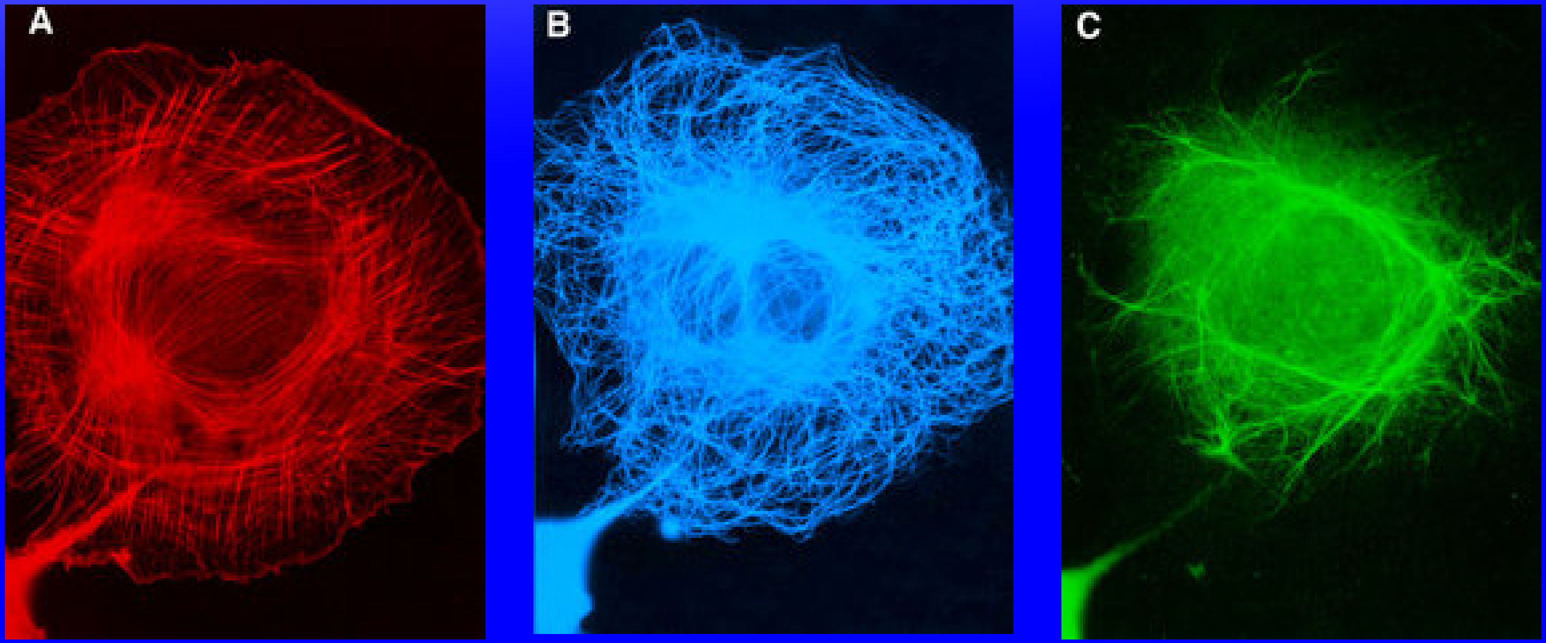
Session 16

SEMIFLEXIBLE POLYMER NETWORKS

Recall: Cytoskeleton

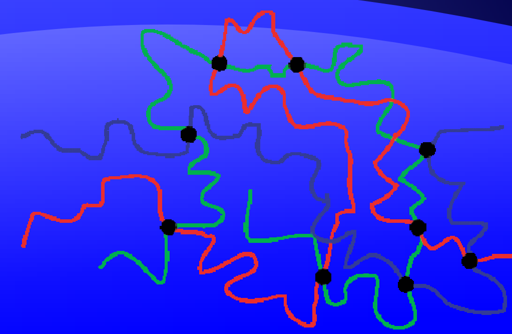
- Three fundamental cytoskeletal filaments

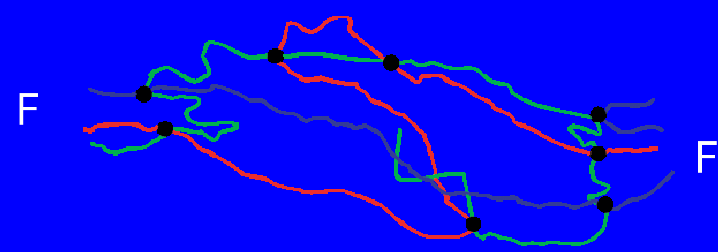


Actin | Microtubules (MT) | Intermediate Filaments (IF)

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
  - (What if you add heat back in?)





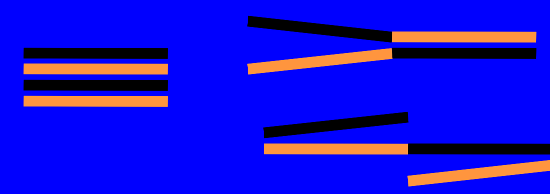
$$F = dU/dl - T\,dS/dl$$

$$F = 0 - T\,dS/dl$$

Entropy of Filaments

- Consider four-segment polymer

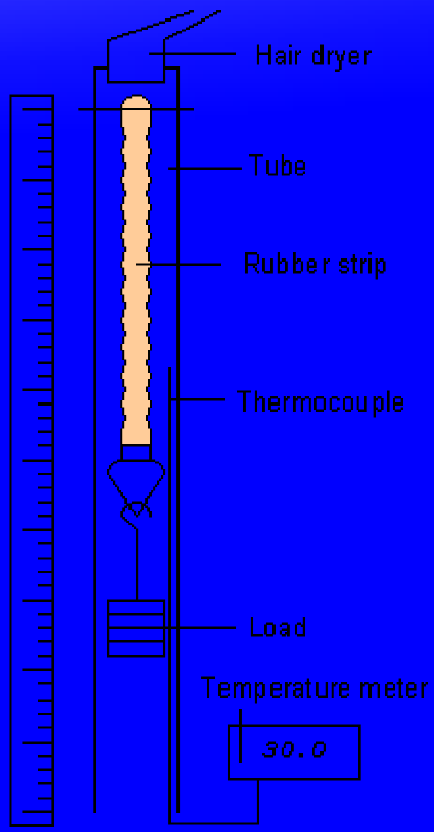
- There are 16 unique configuration states
  - S ≈ ln(16) = 2.77
- There tension is applied such that there cannot be zero separation from end-to-end
  - S ≈ ln(10) = 2.30

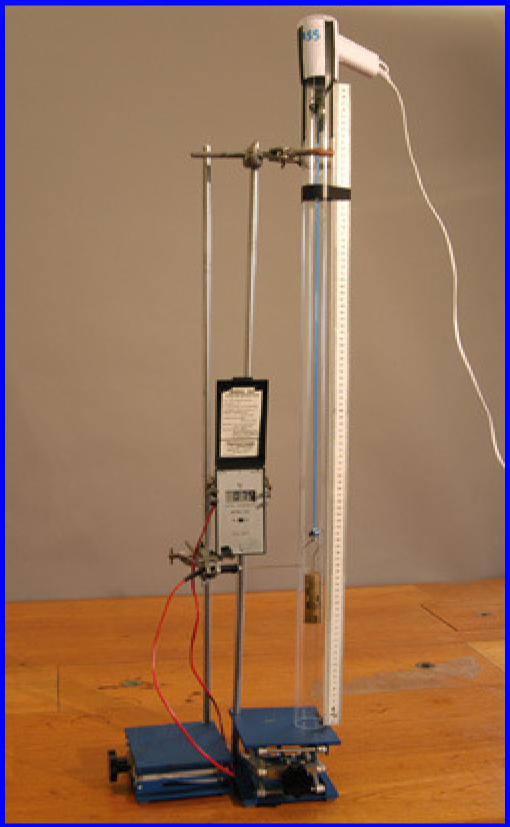


- Therefore, tension reduces entropy

Fun Experiment

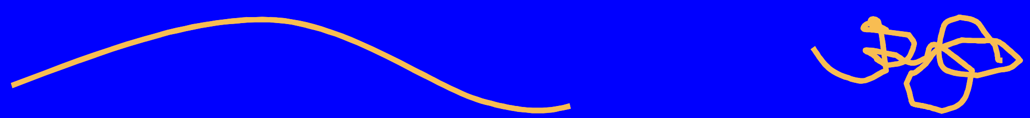
- Entropic stiffness is proportional to temperature





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

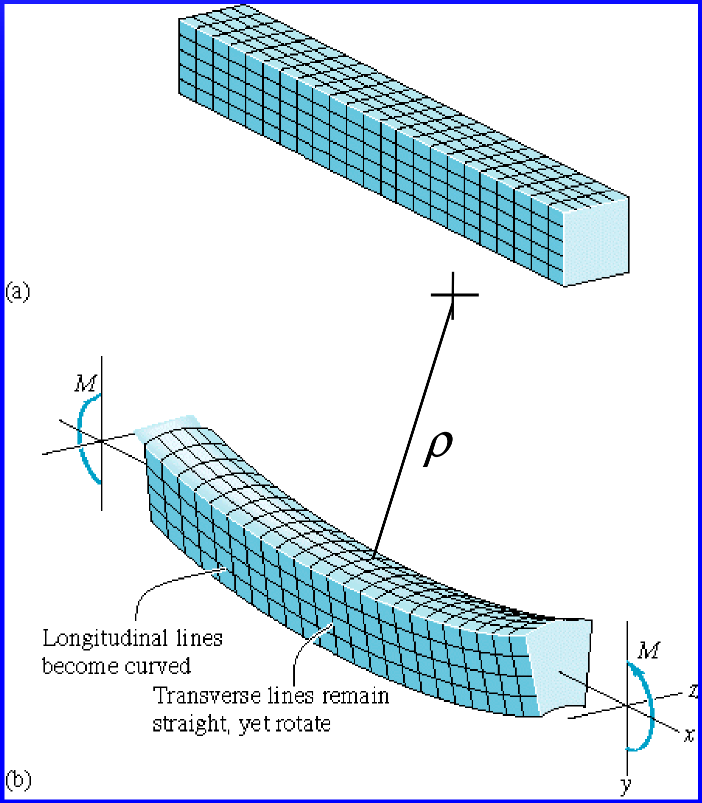
$\kappa = E_Y I$ is bending stiffness

$k = 1.38 \times 10^{-23}$ 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



- Strain Energy

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

- Strain Energy per volume

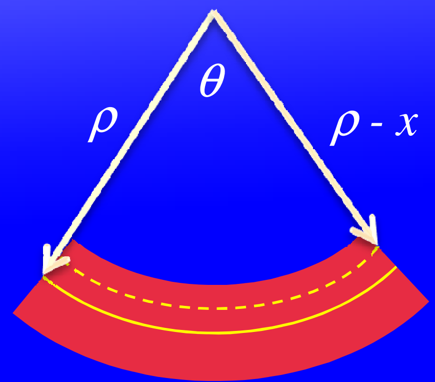
$$U = \frac{W}{V} = \frac{1}{2} \sigma_x \varepsilon_{xx}$$

- By Hooke's Law

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

Bending Curvature

- Interior bending lengths



$$L_{NA} = \rho\theta$$

$$L' = (\rho - x)\theta$$

- 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

$$E = \int_A \frac{1}{2} E_Y \frac{x^2}{\rho^2} dA$$

$$= \frac{1}{2} \frac{E_Y}{\rho^2} \int_A x^2 dA$$

$$= \frac{1}{2} \frac{E_Y I_y}{\rho^2}$$

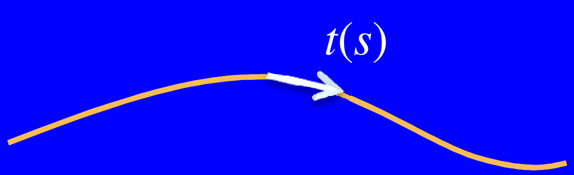
$$= \frac{\kappa}{2} \frac{1}{\rho^2}$$

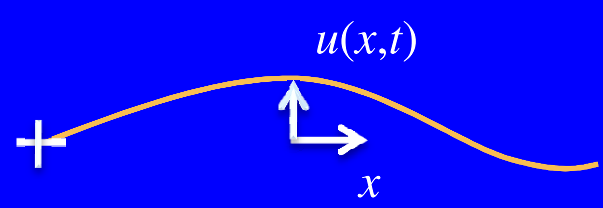
Worm-like Chain Model

- 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

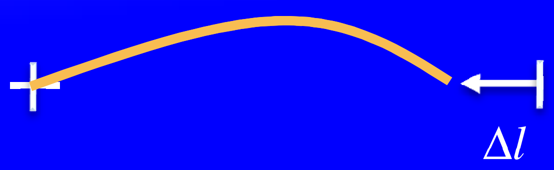
$$H_{bend} = \frac{\kappa}{2}\int_l \left(\frac{\partial \vec{t}}{\partial s}\right)^2 ds$$

- 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 filament measured by amount of extension along a line



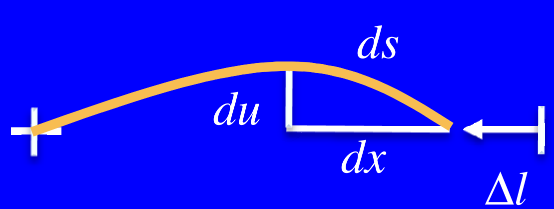
- Extension response dominated by entropy
- At any finite temperature, there is contraction due to thermal fluctuations that make polymer deviate from straight line

Force – Extension Behavior

- Semiflexible chain stretched by tension τ
  - Energy of bending H_{bend}
  - Energy of contraction against τ

- Derive the "shortening" in the filament:

Length is unchanged by kT, τ



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

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 transverse motion direction version

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 compliance is smaller than transverse

Force – Extension Behavior

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

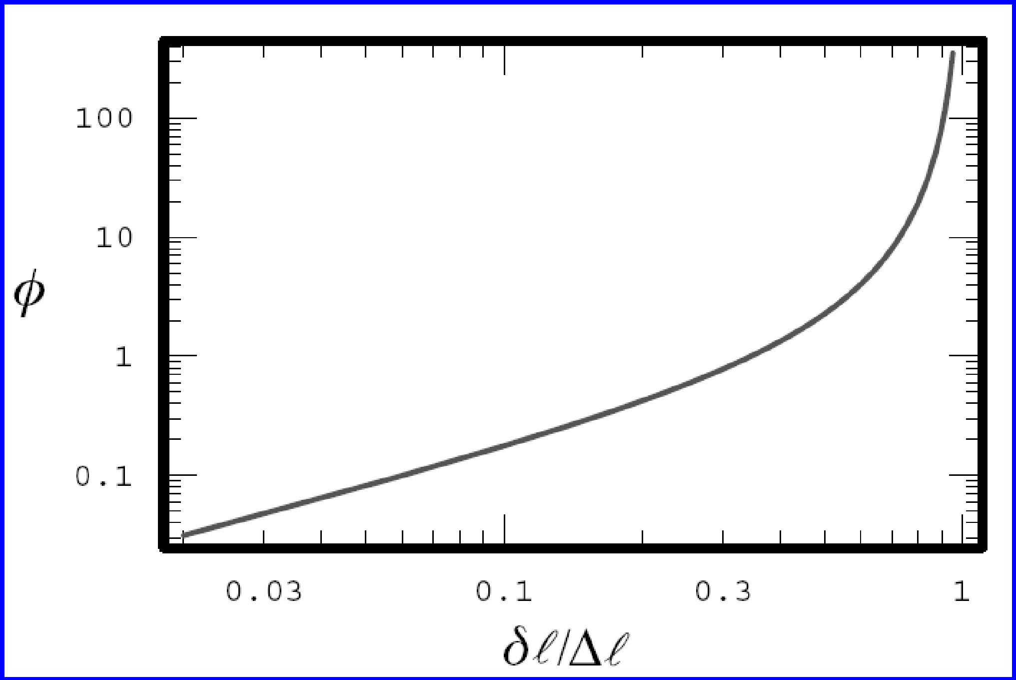
$$\delta l = \frac{kT}{\pi^2}\frac{l^2}{\kappa}\sum_n \frac{\phi}{n^2\left(n^2+\phi\right)}$$

with dimensionless force

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

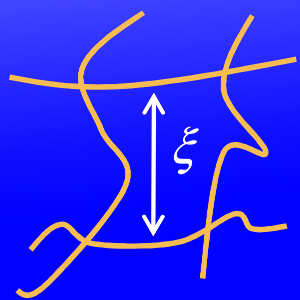
Force - Extension

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

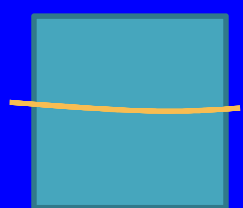


Polymer Interactions

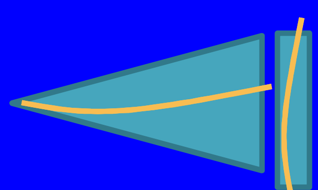
- Solution of polymers have mesh size dimension ξ



  - Typical spacing between filaments
  - Estimated by volume fraction ψ
  - 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

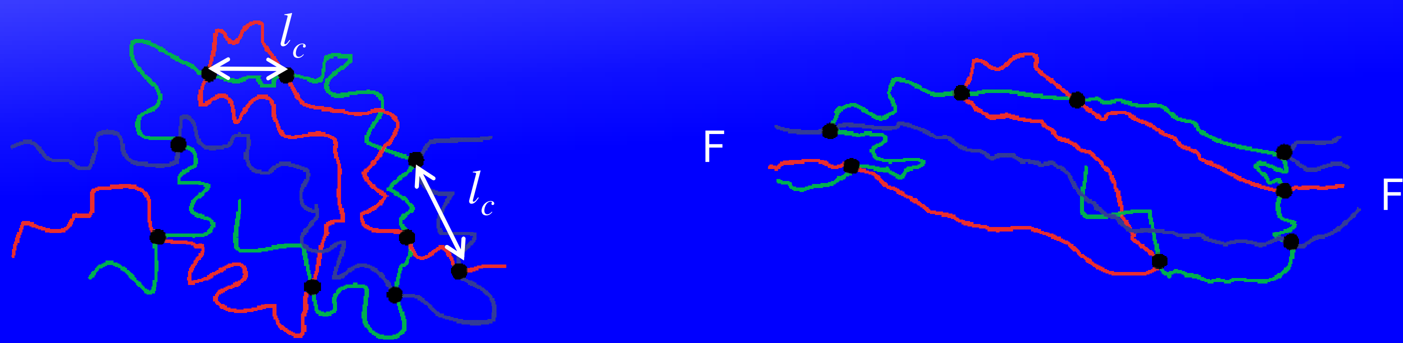
- High frequency testing
  - Filaments not able to relax from high bending modes
  - Increased stiffness from less compliant filaments

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

ρ is polymer concentration, ζ is hydrodynamic drag (per unit length) , η is viscosity

Shear Modulus for Networks

- Consider cross-linking distance l_c



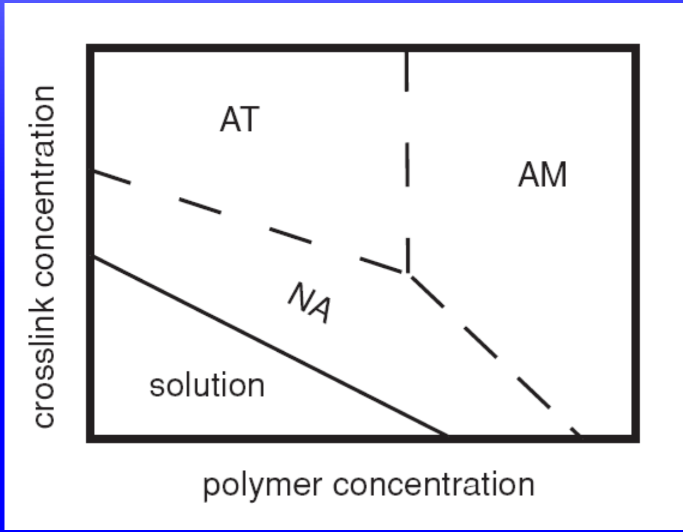
- Deformation types
  - <u>Affine network models</u>: uniform rotation or stretching
  - <u>Non-affine models</u>: macroscopic strains vary from one region to another

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 μ

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