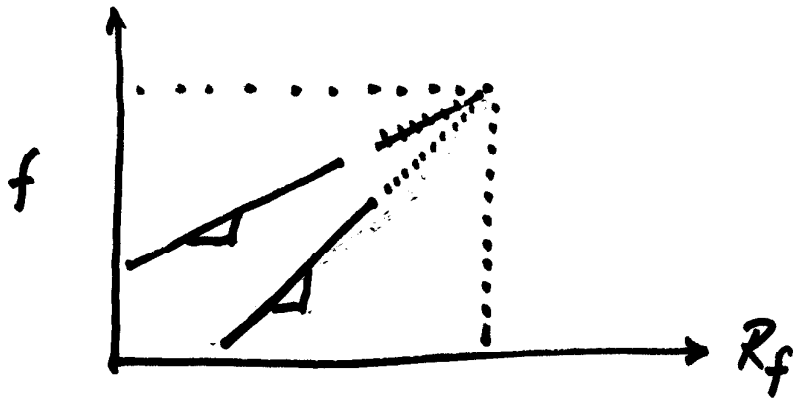
Lecture
10/23/02

Cont'd with Tension blob

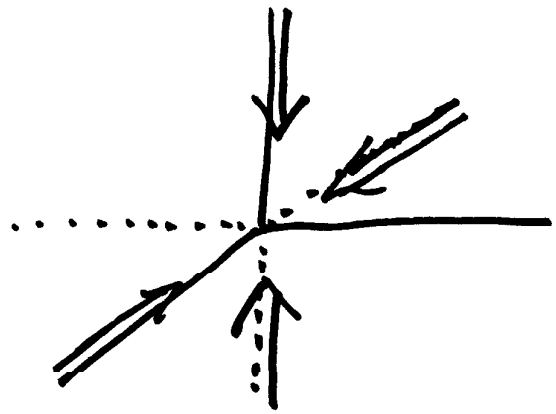
	Ideal	Real
	$A(N, R_f) \approx kT\left(\frac{N}{g}\right)$	$A(N, R_f) \approx kT\left(\frac{N}{g}\right)$
	$\approx kT\left(\frac{R_f}{R_0}\right)^2$	$\approx kT\left(\frac{R_f}{R_f}\right)^{5/2}$
Force	$f \approx \frac{kT}{\xi} \approx kT\left(\frac{R_f}{R_0^2}\right)$	$f \approx \frac{kT}{\xi} \approx kT\,\frac{R_f^{3/2}}{R_f^{5/2}}$
	$\approx \frac{kT}{R_0}\left(\frac{R_f}{R_0}\right)$	$\approx \frac{kT}{R_f}\left(\frac{R_f}{R_f}\right)^{3/2}$

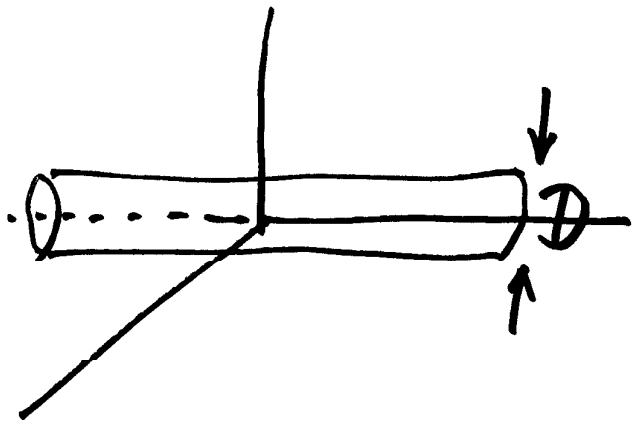
Difference

Reduced force $f/\left(\frac{kT}{b}\right)$	$\frac{fb}{kT} \approx \frac{R_f}{Nb}$	$\frac{fb}{kT} \approx \left(\frac{R_f}{Nb}\right)^{3/2}$
	$R_f << Nb$	$R_f << Nb$



Biaxial compression, confinement in a Tube





	Ideal	Real
$\xi < D$	$D \approx b g^{1/2}$	$D \approx b g^{3/5}$
	$g \approx (D/b)^2$	$g \approx (D/b)^{5/3}$

Constraint:

$$R_F \approx v^{1/5} b^{2/5} N^{3/5}$$
$$\approx b^{3/5} b^{2/5} N^{3/5}$$
$$\uparrow \quad v \approx b^3$$

(athermal limit)

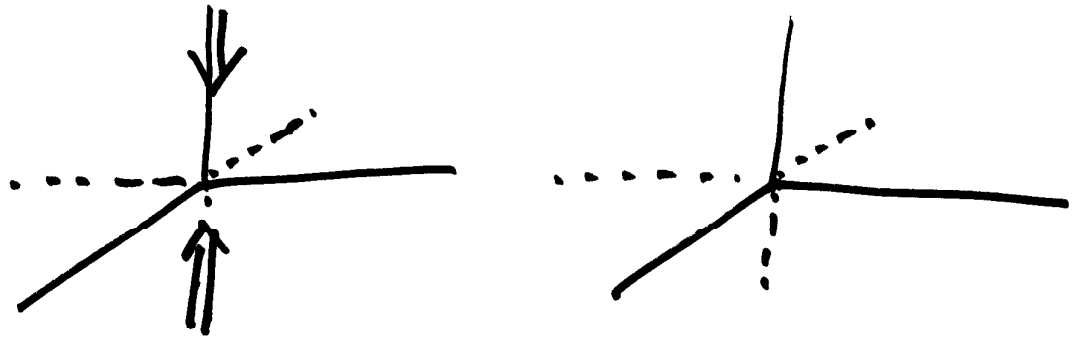
$$R_{||} \approx D\left(\frac{N}{g}\right)^{1/2} \approx bN^{1/2}$$

$$R_{||} \sim N^{1/2}$$

$$R_{||} \approx D\left(\frac{N}{g}\right) \approx \frac{DN}{(D/b)^{5/3}}$$
$$\approx \left(\frac{b}{D}\right)^{2/3} Nb$$

$$R_{||} \sim N$$

Helmholtz Free Energy of Uniaxial Compression



Real Chain: Area occupied by a chain $R_{\parallel}^2$

Energetics: $kT D^2 (N/g)^2 / R_{\parallel}^2$

↑ area/blob

Entropy: $kT R_{\parallel}^2 / (N/g) D^2$

$$\left(\frac{\partial A}{\partial R_{\parallel}}\right) = 0, \quad R_{\parallel} \approx D\left(\frac{N}{g}\right)^{3/4} \approx N^{3/4} b \left(\frac{b}{D}\right)^{1/4}$$

Chain dimension under compression by parallel plates

$R_{\parallel} \sim b N^{1/2}$ (ideal)

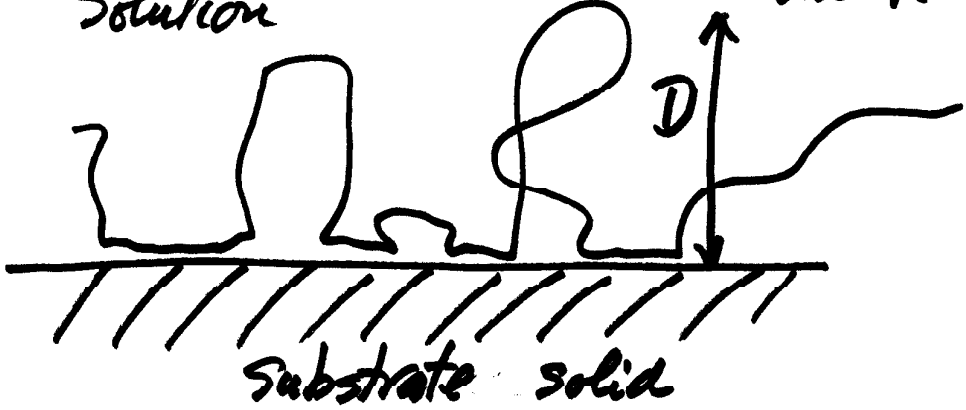
$R_{\parallel}^{real} > R_{\parallel}^{ideal}$ – Excluded volume effect!

Chain Adsorption on a Substrate.

Energy/monomer $\approx -\varepsilon kT$

$0 < \varepsilon < 1$

Weak adsorption limit

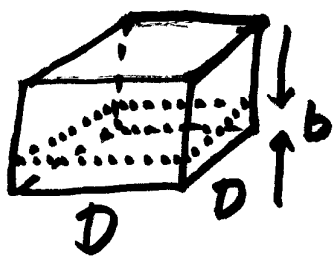


Adsorbed thickness

$D < R$

	Ideal	Real
	$D \approx b g^{1/2}$	$D \approx b g^{3/5}$ (athermal)
	$g \approx (D/b)^2$	$g \approx (D/b)^{5/3}$
vol fraction within a blob	$\phi \approx \frac{b^3 g}{D^3}$	$\phi \approx \frac{b^3 g}{D^3}$
	$\approx b/D$	$\approx (b/D)^{4/3}$

# of monomer in contact with the surface



ϕ/b^3 = # density of monomer within a blob w/ D

Adsorbed layer volume with a monomer thickness b

$= D^2 b$

$$\frac{\phi}{b^3} \cdot D^2 b$$

Ideal

$$\frac{\phi}{b^3} \cdot D^2 b \approx D/b$$

$$\varepsilon kT \cdot \frac{D}{b} \approx kT$$

$$D \approx b/\varepsilon$$

Real

$$\frac{\phi}{b^3} D^2 b \approx (D/b)^{2/3}$$

$$\varepsilon kT \left(\frac{D}{b}\right)^{2/3} \approx kT$$

$$D \approx b/\varepsilon^{3/2}$$

$D^{real} > D^{ideal}$ ($\varepsilon < 1$)

Free Energy

$$A_{ads} \approx -kT\left(\frac{N}{g}\right) \approx -kTN\varepsilon^2$$

$$A_{ads} \approx -kT\left(\frac{N}{g}\right) \approx -kTN\varepsilon^{5/2}$$

$|A_{ads}^{real}| < |A_{ads}^{ideal}|$ ($\varepsilon < 1$)