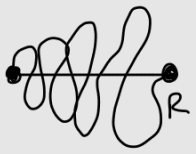
Force-extension of polymer chain



$$F(N,R) = \frac{d\,k_BT}{2}\left(\frac{R}{R_0}\right)^2 \quad , \quad \text{for ideal chain } R_0 = l_K N^{\nu_2}$$

now,

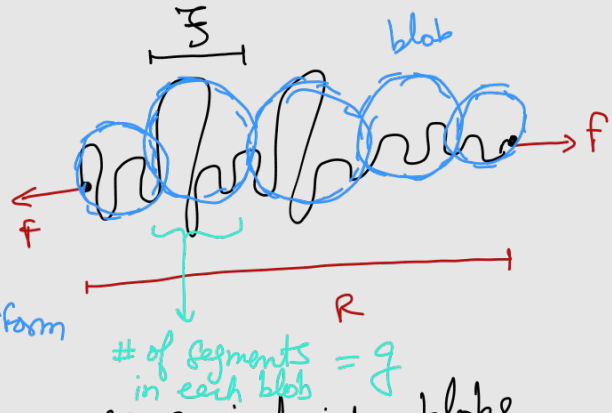
force is the derivative of free energy w.r.t R (the same ways Pressure is a derivative of free energy w.r.t volume)

$$\text{force}: \quad f = -\frac{dF}{dR} = \underbrace{\left(\frac{d\,k_BT}{R_0^2}\right)}_{\text{spring constant}} R$$

$\therefore$
- high temp. $\Rightarrow$ higher the spring constant $\Rightarrow$ stiffer the polymer
- long polymer (high R_0) $\Rightarrow$ lower spring constant $\Rightarrow$ the softer the polymer.

we'll try to re-derive this with only the physical / scaling argument

- if there's fixed tension (on average) in the chain, then the distribution of monomers along the chain must be uniform



$\Rightarrow$ the chain can be coarse-grained into blobs.

* monomer length $= b$

$(b = l_K)$

Rubenstein notation

Saarloos notation

* k_BT energy per blob

* factors that determine size of the blob
  - by stretching we are restricting the direction each blob can have.

* inside the blob, the chain must have statistics of ideal chain.

* we only care about the scaling, so through this discussion, pre-factors will not be used

- $\xi \approx b g^{1/2}$ (same as $R_0 = l_K N^{1/2}$ but applied to the blob instead of segment)

- also,

R = size of the blob × number of blob (look at the polymer figure on prev. page)

$\approx \xi \times \frac{N}{g}$ → total number of monomers
→ number of monomers in 1 blob.

plug in g from prev. eqn ($\xi = b g^{1/2}$):

$$R \approx \frac{N b^2}{\xi}$$

$$g \approx \frac{N^2 b^2}{R^2}$$

→ no need to distinguish between segment length (ξ_g), or kuhn length or monomer length (b)

also,

free energy : $F \approx$ free energy per blob $\times$ # of blobs

$$\therefore F \approx k_B T \frac{N}{g} \approx k_B T \frac{R^2}{Nb^2} \approx k_B T \left(\frac{R}{R_0}\right)^2$$

$$\boxed{F \approx k_B T \left(\frac{R}{R_0}\right)^2}$$

* we got the same expression for free energy as the one we got from counting # of steps in prev. lecture $\left(\frac{d k_B T}{2}\left(\frac{R}{R_0}\right)^2\right)$, only by dimensionality and physical / scaling arguments.

Real self avoiding walk

when force is 0,

$$\boxed{R_F \approx b N^{\nu}} \quad , \nu = 3/5$$

Flory length (new variable introduced by Kuhn for size of the polymer)

✗ is $F \approx k_B T \left(\frac{R}{R_F}\right)^2$? [i.e. naively replace R_0 in the denominator with R_F in the expression of F for an ideal chain]

here $\boxed{\xi \approx b g^{3/5}}$ (instead of $g^{1/2}$)

$$R \approx \xi \frac{N}{g} \approx \frac{N b^{5/3}}{\xi^{2/3}}$$

replacing N (from $R_F = b N^{3/5}$)

$$\Rightarrow \boxed{R \approx \frac{R_F^{5/3}}{\xi^{2/3}}}$$

$$\therefore \quad \boxed{\zeta = \frac{R_f^{5/2}}{R^{3/2}}}$$

free energy expression would still be valid:

$$F \approx k_B T \frac{N}{g} \approx k_B T \frac{R}{\zeta}$$

$$\approx k_B T \left(\frac{R}{R_f}\right)^{5/2}$$ → ideal chain is squared $\left(\frac{R}{R_0}\right)^2$

* our guess is not supported by this scaling argument "derivation" of free energy.

→ Real/Non-ideal chain is a non-linear spring.

$$\boxed{f = -\frac{dF}{dR} \approx k_B T \left(\frac{R}{Nb}\right)^{3/2}}$$

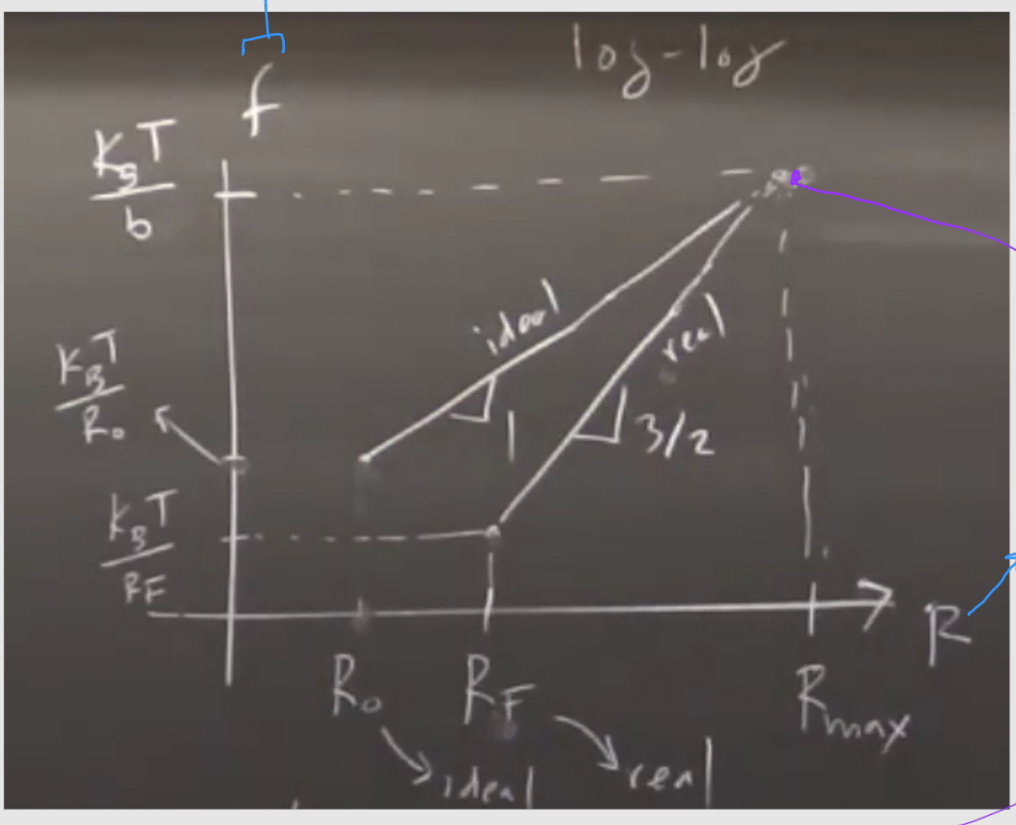
(using the fact that $R_f = bN^{3/5}$)

* Based on this, is it easier to stretch a self avoiding real chain as compared to an ideal chain?

$y = a x^b$

$\log y = \log a + b \log x$

Force V/S polymer size



* Scaling arguments assume each blob has many monomers.
  - >> when polymer is fully stretched, there's only one blob (containing the entire chain), so this is only valid upto ($R = R_{max}$)

* ideal chain is more compact but also stiffer compared to a real chain

Polymer Solvents

- from Flory argument, we defined excluded volume parameter V. Here it must be equal to the monomer size: $V \approx b^3$

* v can be negative or positive in a solution

1.) Negative if monomers are sticky to each other.

2.) Positive if repulsive interaction b/w monomers

monomers don't like to be on top of each other

monomers like solvent more than themselves

solvent Same nature as the monomers.

monomers are sticky

collapse into itself with no solvent in it.

This is the case of *athermal solvents*. In many cases, there can be some stickiness between monomers, which can depend on temperature (see Rubinstein and Colby, 3.1)

$v = b^3$	*athermal solvent*
$0 < v < b^3$	*good solvent*
$v = 0$	*θ solvent*
$-b^3 < v < 0$	*poor solvent*
$v = -b^3$	*non solvent*

Flory argument: $R_F \approx (vb^2N^3)^{\frac{1}{5}}$

$R_{ideal} \approx bN^{\frac{1}{2}}$

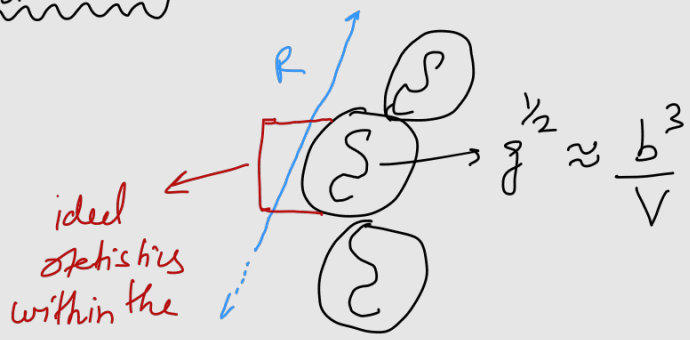
$R_F > R_{ideal}$ when $(vb^2N^3)^{\frac{1}{5}} > bN^{\frac{1}{2}} \Rightarrow N > \frac{b^6}{v^2}$

Chain swells when N is sufficiently large

What is the chain coil size as a function of v?

→ Chain size vs solvent quality (V)

1) Good solvent $(0 < v < b^3)$



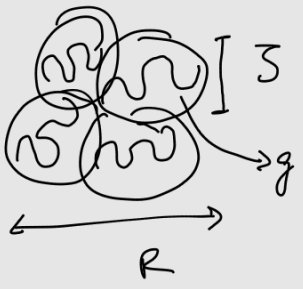
* SAW:
Self avoiding walks

SAW of blobs.

$$\xi \approx b g^{1/2} \approx \frac{b^4}{V}$$

$$\Rightarrow \quad R = \xi \left(\frac{N}{g}\right)^{3/5} \approx b \left(\frac{V}{b^3}\right)^{-1/5} N^{3/5}$$

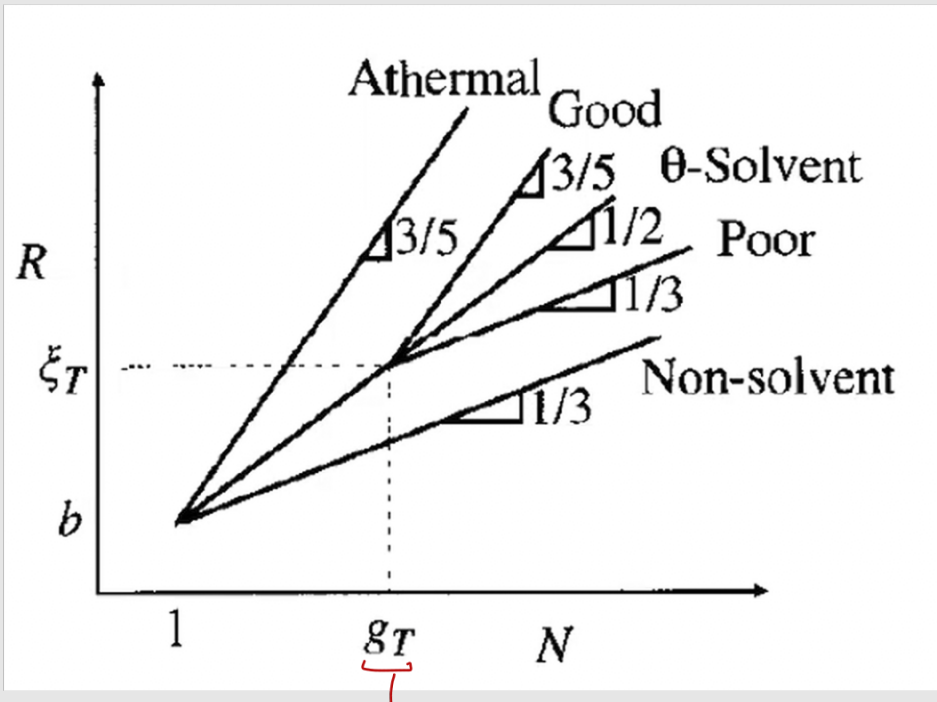
2) Poor Solvent



$$R \approx \xi \left(\frac{N}{g}\right)^{1/3}$$

$$V \approx R^3 \approx \left(\frac{N}{g}\right) \xi^3$$

Polymer swelling v/s degree of polymerisation in different solvents.



g_T → thermal blob size

Expression of excluded volume parameter as a function of temperature

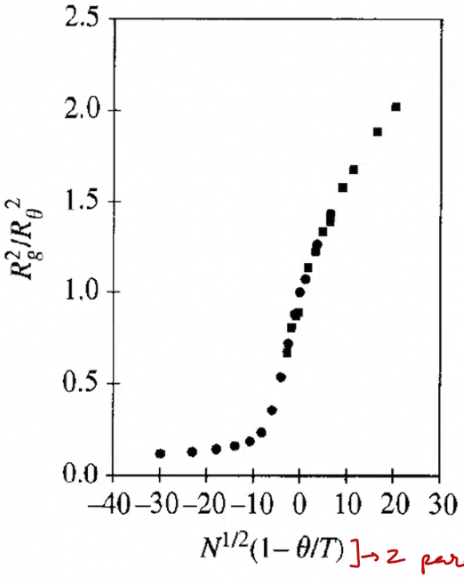
typically,

$$v \approx \frac{T-\theta}{T} b^3$$

* HW

Have a look in Rubenstein or any other book about how one can calculate excluded volume interaction by integrating the potential energy of interaction between the monomers

"Coil to globule transition"



→ 2 parameters.

$$z \approx \frac{T-\theta}{T} N^{1/2}$$

$$\frac{R}{bN^{1/2}} \approx \frac{b}{|v|^{1/3} N^{1/6}} \approx |z|^{-1/3} \quad \text{for } T < \theta$$

$$\frac{R}{bN^{1/2}} \approx z^{2\nu-1} \quad \text{for } T > \theta$$

Flory exponent ($\frac{3}{5}$)

Monte Carlo simulations of Lennard-Jones chains
Graessley et al. 1999