# Basic Polymer Science

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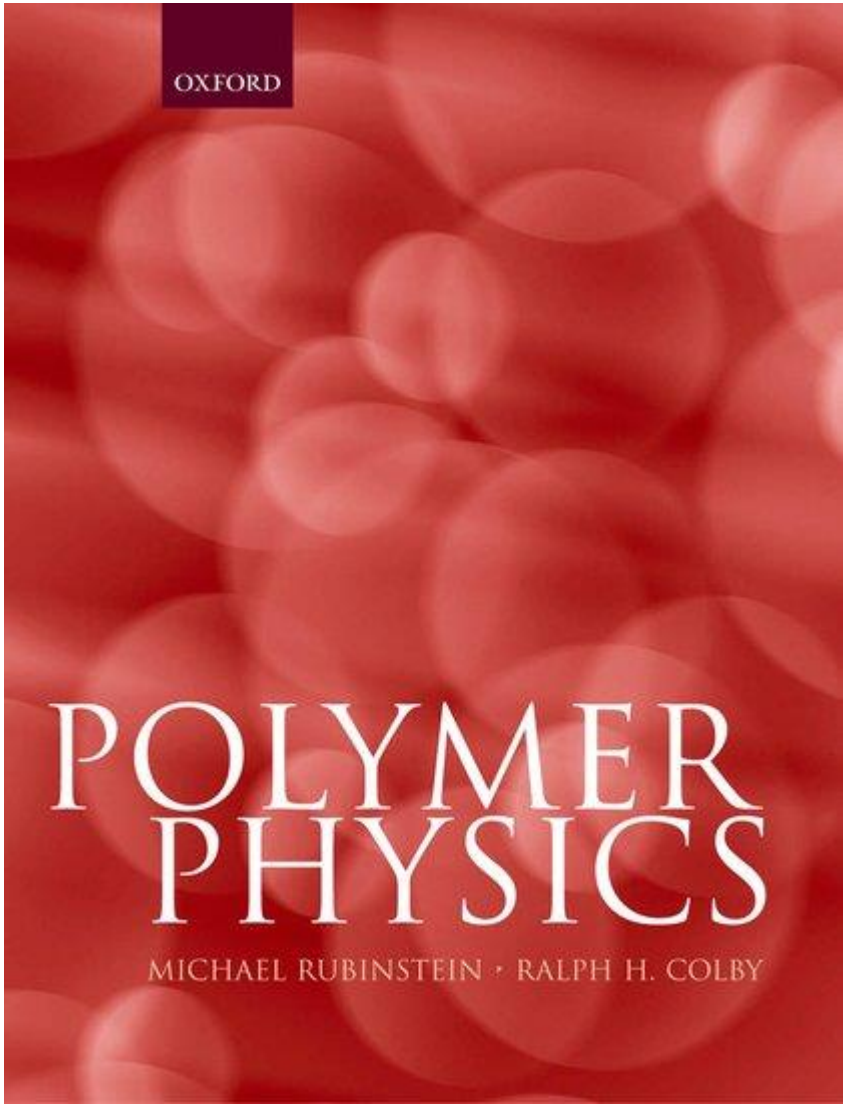
# Recommended book

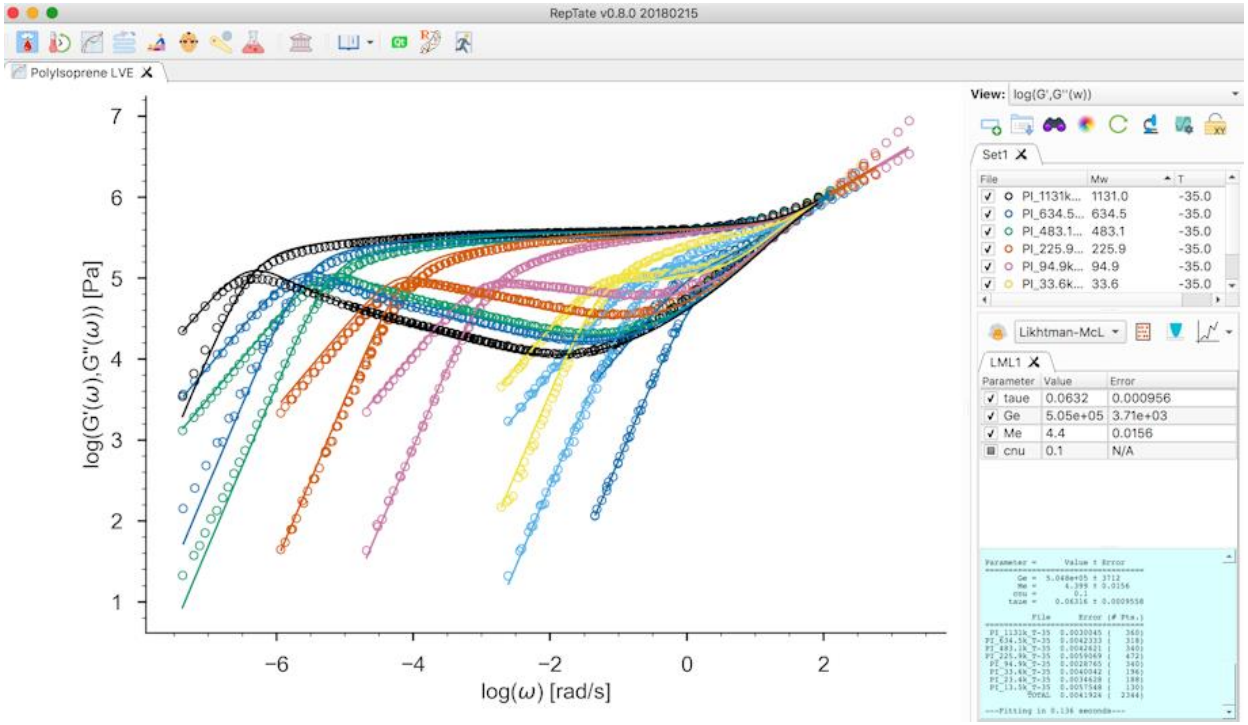


# Adverts!

Useful software for rheology: **Reptate**

https://reptate.readthedocs.io/

RepTate (Rheology of Entangled Polymers: Toolkit for Analysis of Theory & Experiment) is a free and open source software package for viewing, exchanging and analysing experimental data.

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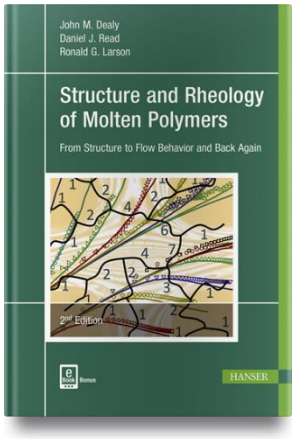


# Overview

Polymers – what are they?

STRUCTURES

- - Kinds of polymer chemistry and structure.
- - Polymers as random walks.
- - Why do polymers phase separate? Ordering and pattern formation.
- - Polymer crystallisation.

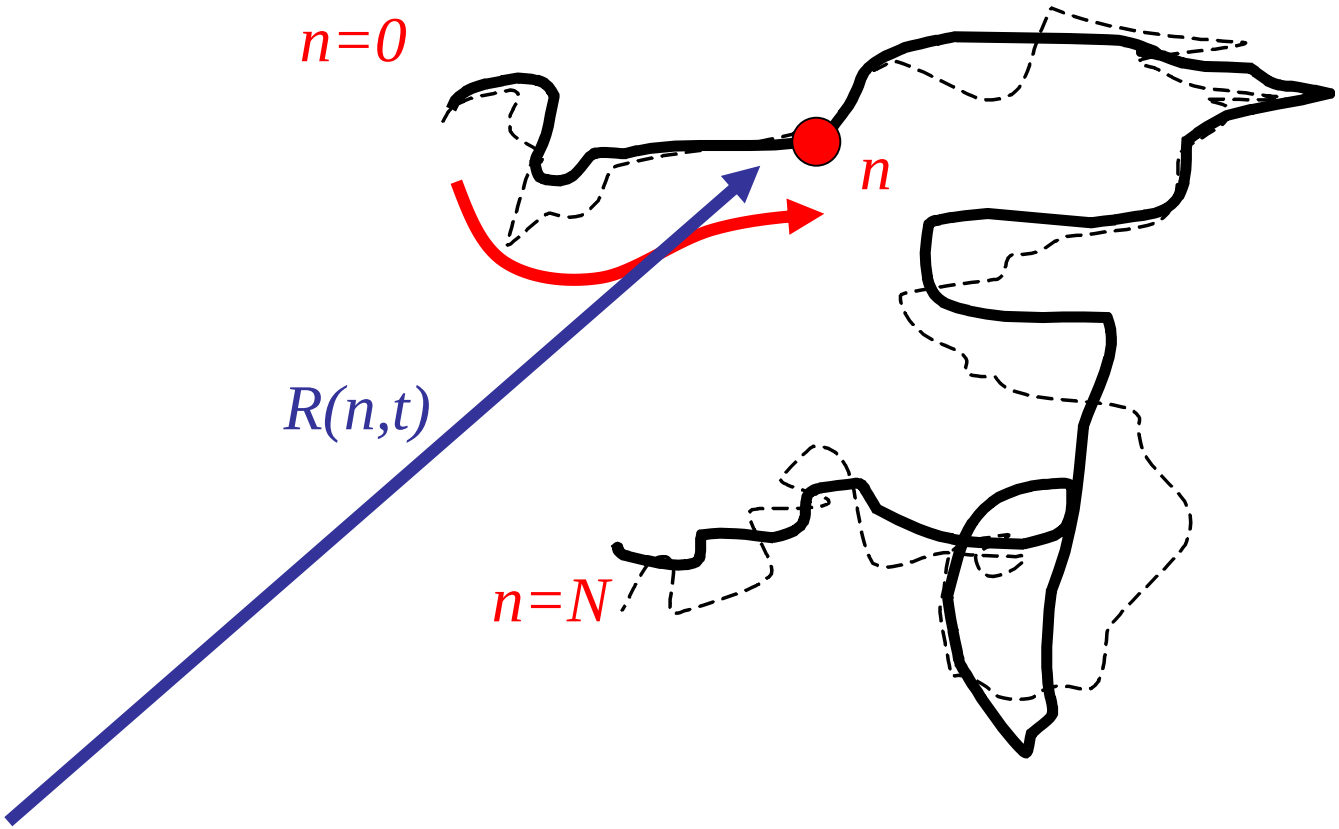
DYNAMICS

- - Slow dynamics, dynamics at different lengthscales, concept of glass transition, experimental measures
- - dynamics and rheology
- - dynamics and phase separation

# Coarse-graining polymers

A standard “trick” of the theoretical physicist is to ignore the local chemical detail of a polymer, and to recognise that polymers are long, string-like molecules.

We think of a linear polymer as being equivalent to a string of *n* beads joined together.



# Polymers as random walks

The first model we use to describe the configuration of the long-stringy molecule is the “random walk”.

$$\left\langle \mathbf{x}_i \cdot \mathbf{x}_j \right\rangle = \begin{cases} 0 & i \neq j \\ b^2 & i = j \end{cases}$$

Each link in the chain has a typical length *b* and takes a step in a direction that is **statistically uncorrelated** with all other steps in the chain.

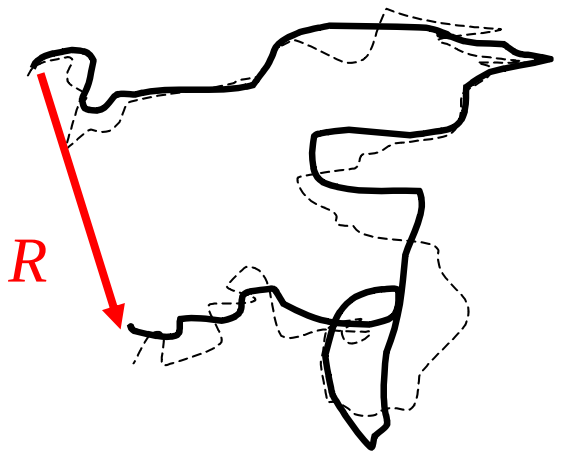
$$\mathbf{R} = \sum_i \mathbf{x}_i$$

Using this model, we can derive the result that the typical size of the molecule increases with the square root of the number of beads.

$$\left\langle \mathbf{R} \cdot \mathbf{R} \right\rangle = \left\langle \sum_i \mathbf{x}_i \cdot \sum_j \mathbf{x}_j \right\rangle$$

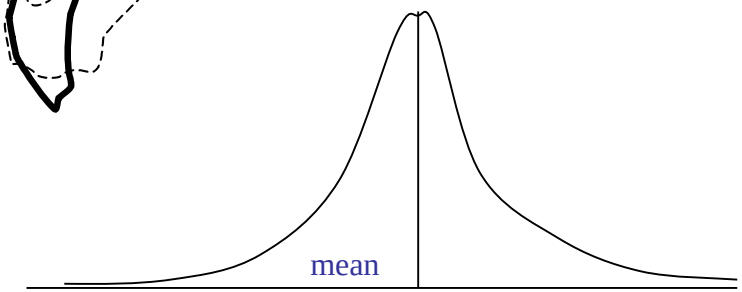
$$= \sum_i \sum_j \left\langle \mathbf{x}_i \cdot \mathbf{x}_j \right\rangle$$

$$= Nb^2$$




We can also show that the probability distribution of the end to end vector is a normal distribution:

$$P(\mathbf{R}) = \left( \frac{3}{2\pi N b^2} \right)^{3/2} \exp\left( \frac{-3R^2}{2Nb^2} \right)$$

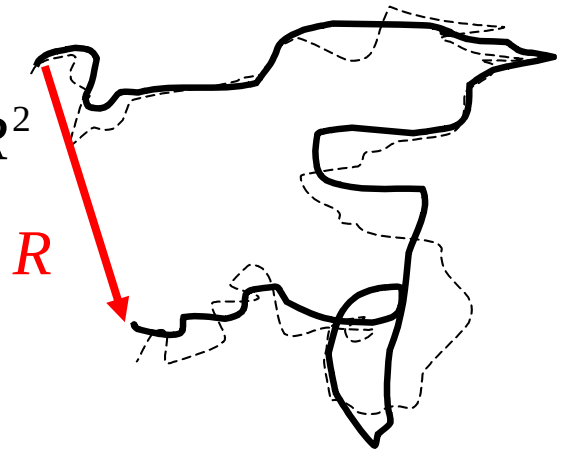


# Springs, forces and stress

Polymer chains are in constant motion due to the thermal energy of their surroundings. If you stretch them out, their thermal motion pushes them back towards a coiled configuration. So, they behave as springs. The spring force, and resulting stress, can be derived using statistical mechanics.

$$P(\mathbf{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(\frac{-3R^2}{2Nb^2}\right)$$

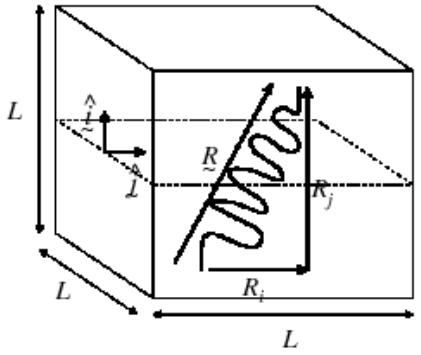
Elastic energy of a chain: $F(R) = -k_B T \ln(P) = \frac{3k_B T}{2Nb^2} R^2$




Force due to a single chain: $f(R) = \frac{3k_B T}{Nb^2} R$

Gives rise to stress....

In linear rheology, modulus is **$k_B T$ x no. of chains/volume**




In general.....

$$\sigma_{ij} = \frac{3k_B T C_{mon}}{N^2 b^2} \langle R_i R_j \rangle$$

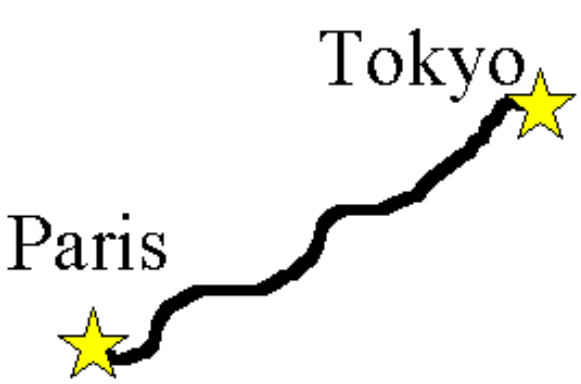
# Polymers as random walks

- So, you shouldn't (usually) think of a polymer chain as being stretched out in a straight line (though chain stiffness, or electrostatics may change that).
- You shouldn't think of a polymer chain as being scrunched up into a ball (although in a bad solvent it might be)
- You should think of it as somewhere between these two extremes – the random walk, a not-very-tightly-packed blob.

***Example:*** $N=10^9$ **and monomer size** $a=1$ *cm*

$L \sim aN \sim 10^7\,m$

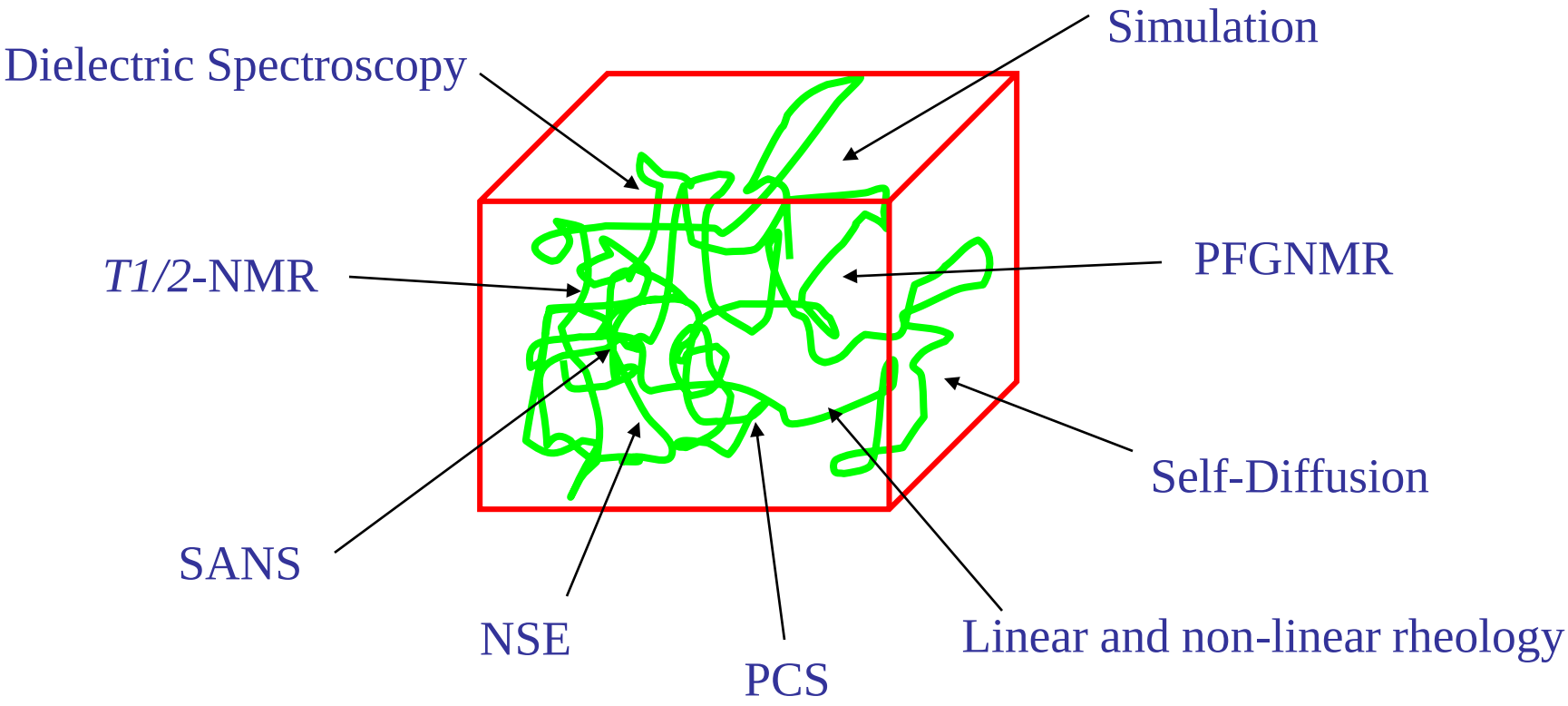
$R \sim aN^{1/2} \sim 10^3\,m$




$R \sim aN^{1/3} \sim 10\,m$

# Experiment
# - techniques that probe polymer dynamics:

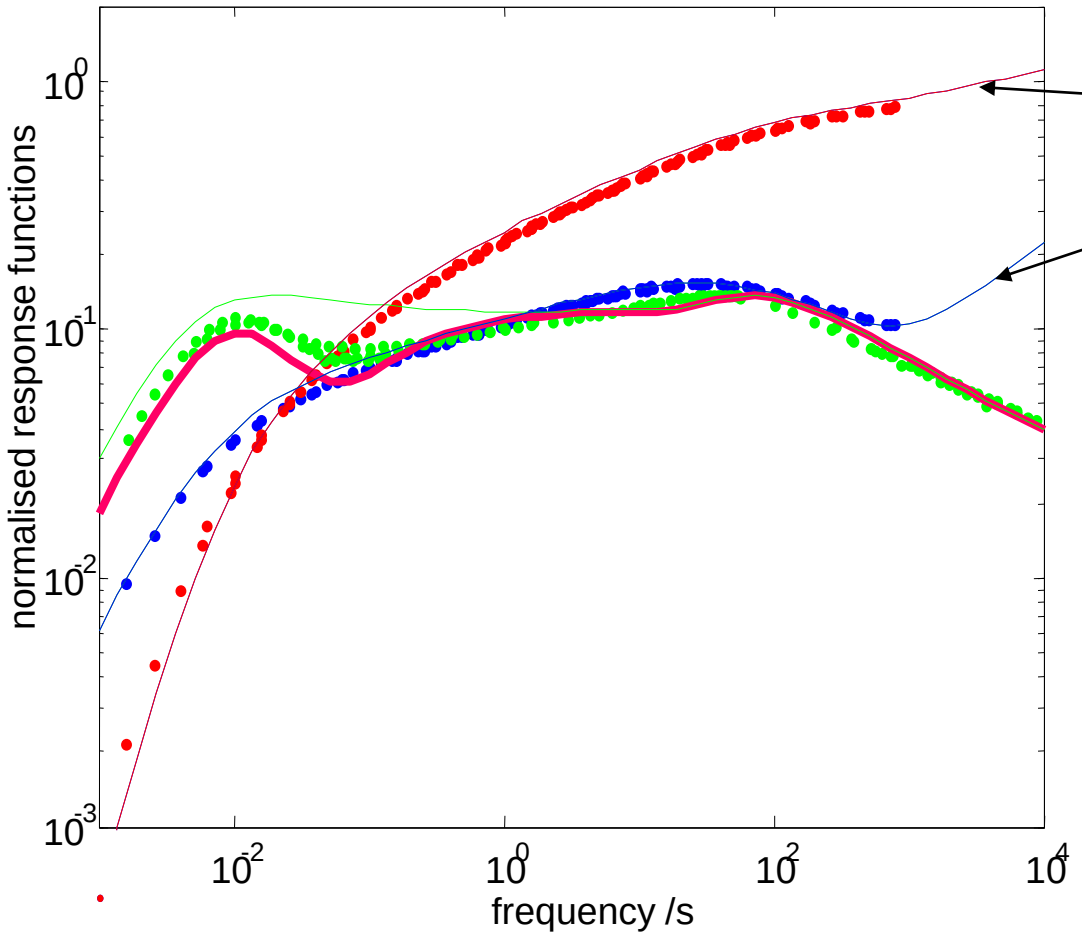
- Bulk information orthogonal to rheology
- Direct Molecular information



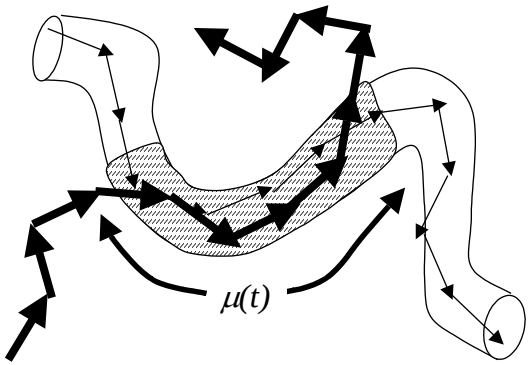
# Dielectric Spectroscopy for Z=16 stars

(Watanabe 2002)

$$\left\langle \frac{\partial R(n',t)}{\partial n'} \frac{\partial R(n,0)}{\partial n} \right\rangle$$



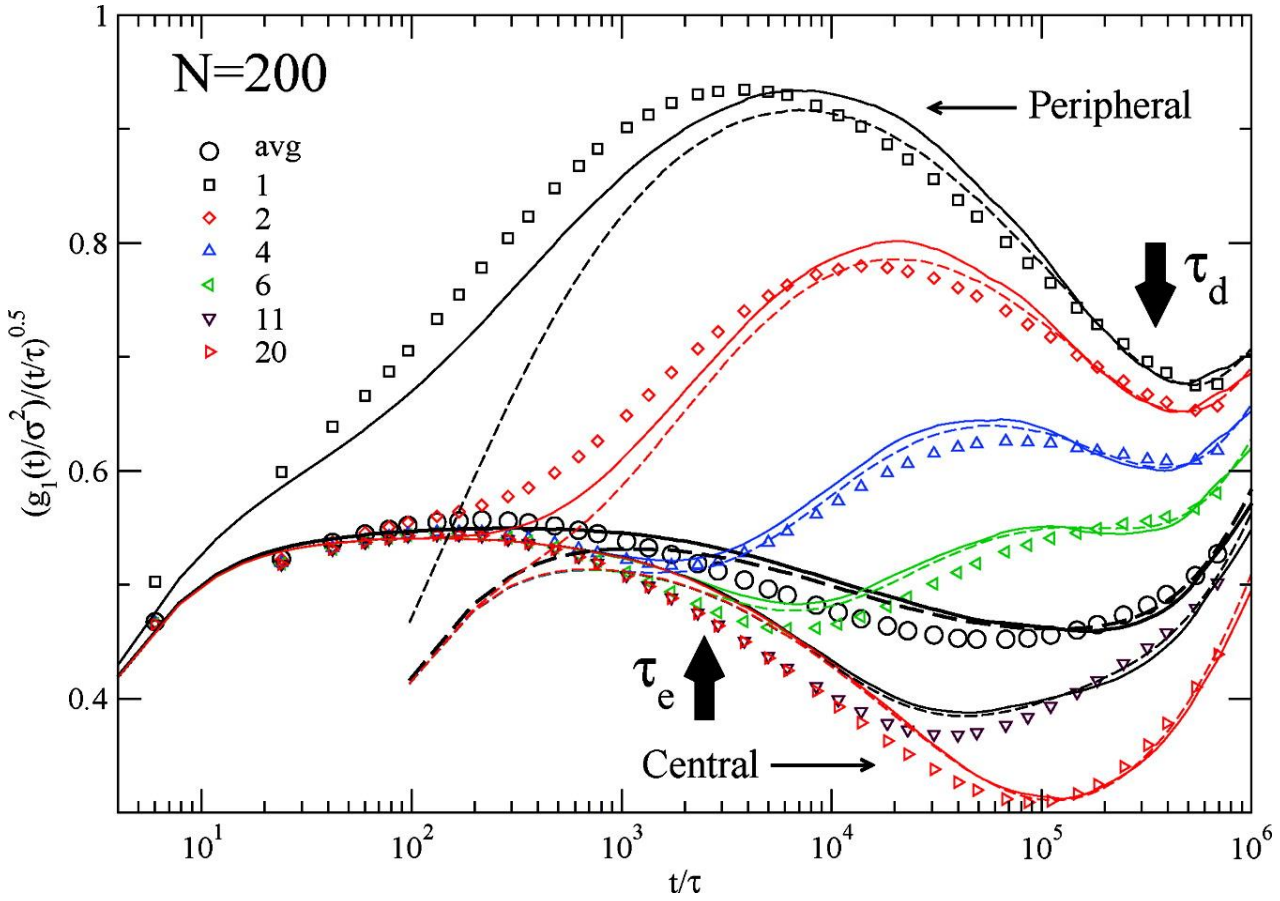

rheology



# Simulation

$$\left\langle \left( \boldsymbol{R}(n,t) - \boldsymbol{R}(n,0) \right)^2 \right\rangle$$

(in this case …)

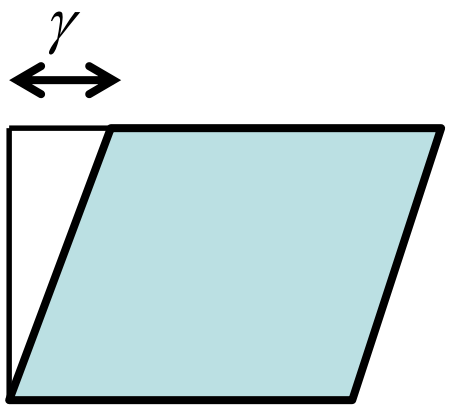



Sukumaran and Likhtman (2009)

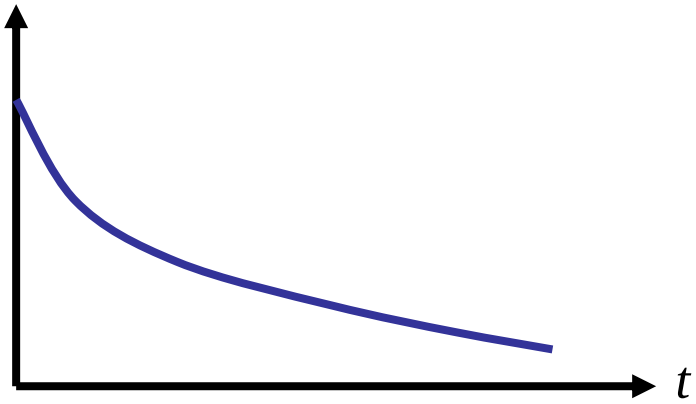
# Linear viscoelasticity

Materials have memory of past deformation.

Following a step strain, the stress decays as:




$$\sigma(t) = \gamma G(t)$$



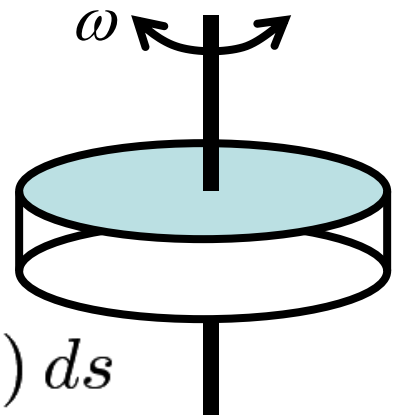

"relaxation modulus"

Viscosity (at low shear rates) obtained from integral over relaxation modulus:

$$\mu = \int_0^\infty G(s)\, ds$$

# Linear viscoelasticity

Usually linear viscoelasticity measured as a function of frequency in oscillatory shear:




$$G^* = G' + iG'' = \int_0^\infty i\omega G(s) \exp(-i\omega s)\, ds$$

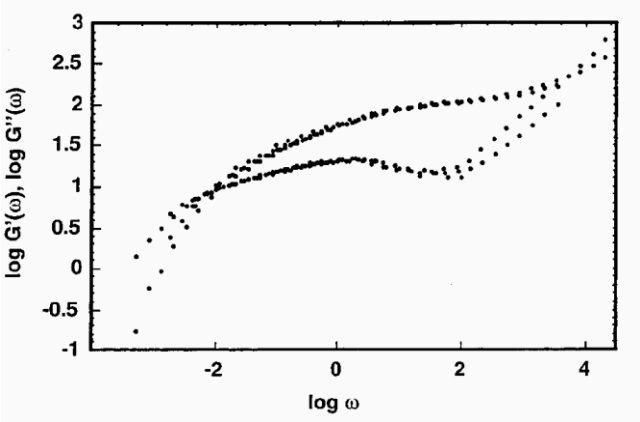
Storage modulus

From component of stress in phase with applied strain

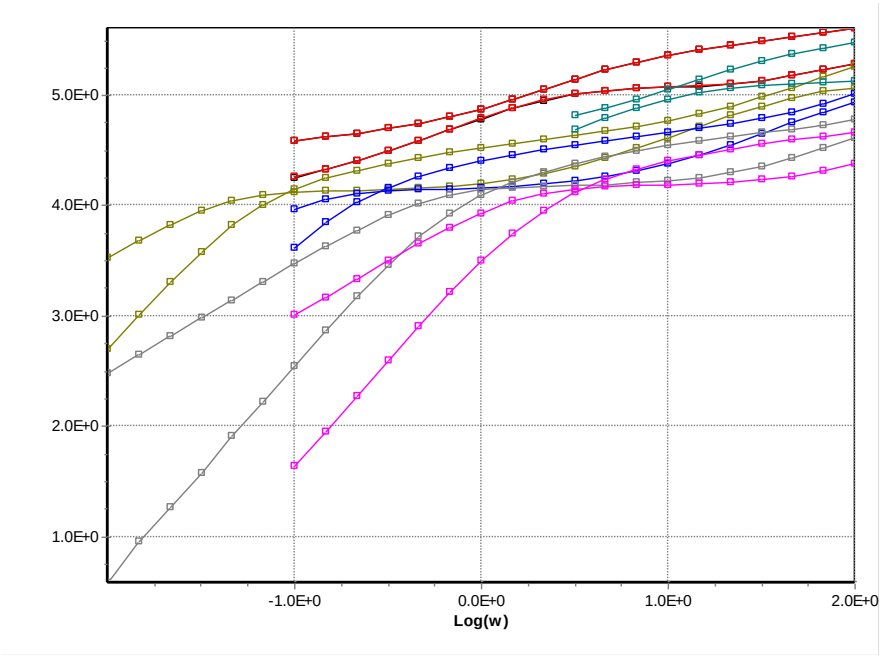
Loss modulus

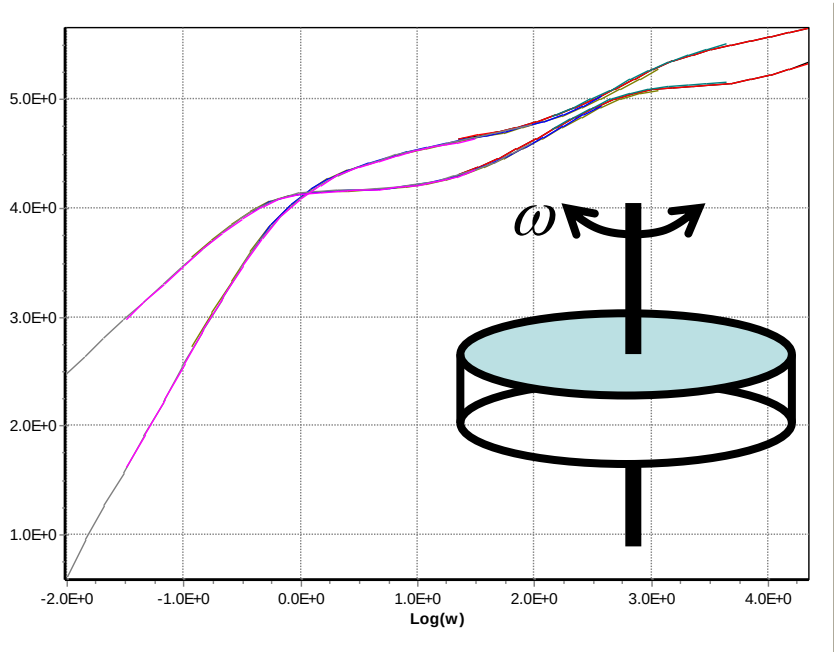
From component of stress in phase with strain rate

Gives a viscoelastic “signature” of the material



# Time-temperature superposition




- In practice, experimental frequency range is limited.
- So, perform experiments at different temperatures.
- If molecular motion depends on a single fundamental process (e.g. monomer motion) then can “time-temperature shift” the data (shift along frequency axis)
- This produces a “master-curve” appropriate to a given reference temperature.

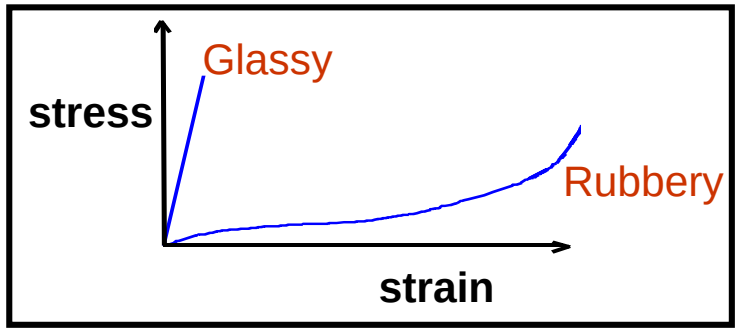
Main messages concerning polymer dynamics:

LENGTHSCALE MATTERS!

(or, polymer structure, and polymer dynamics, go together)

Small sections move quickly, larger things move more slowly.

# Modulus with Temperature

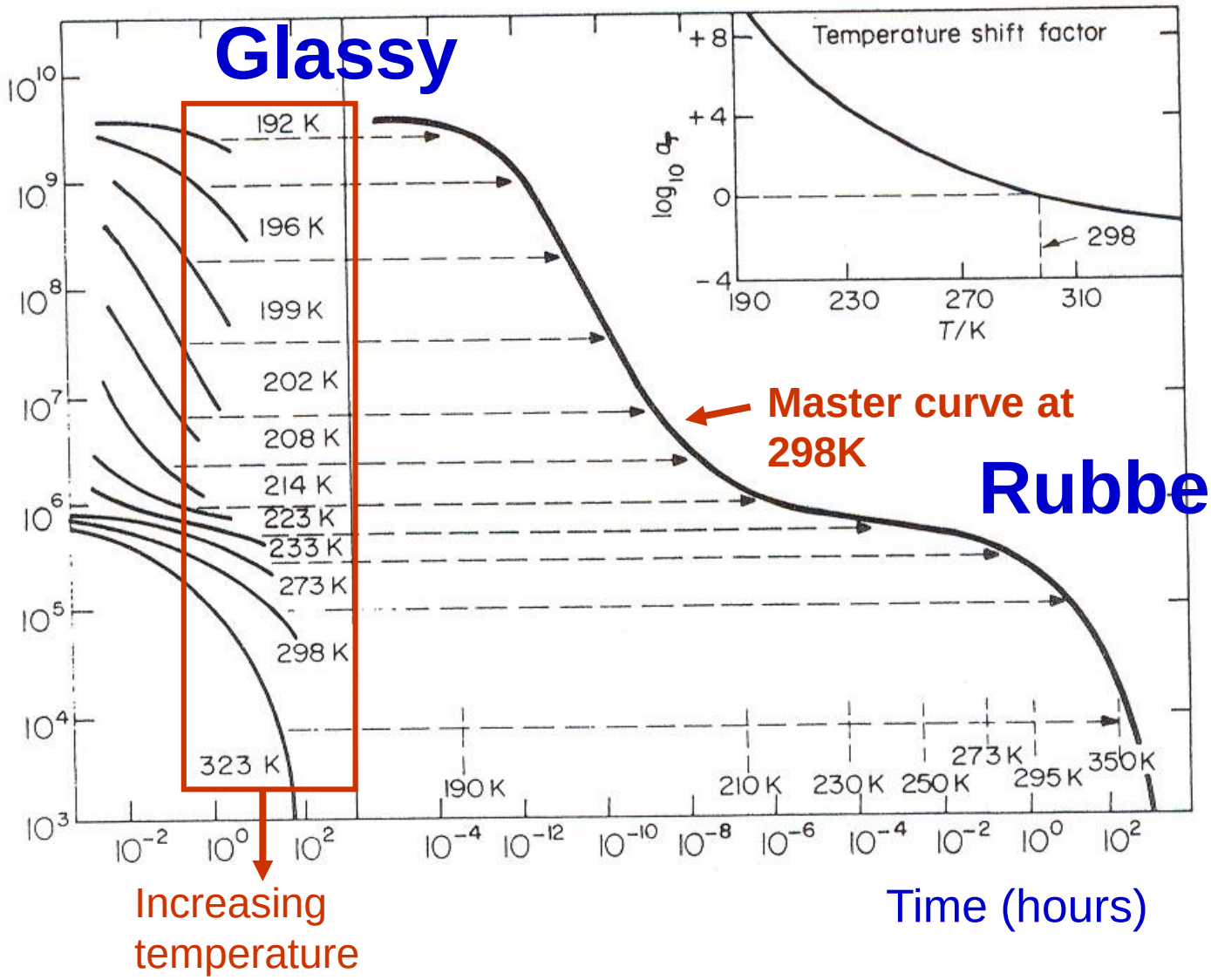






This has to do with dynamics (at the smallest scale), because the question is:
**do the monomers have time for local rearrangements on the timescale of the experiment?**

# Time Temperature Superposition (time domain)



# Rubber Elasticity

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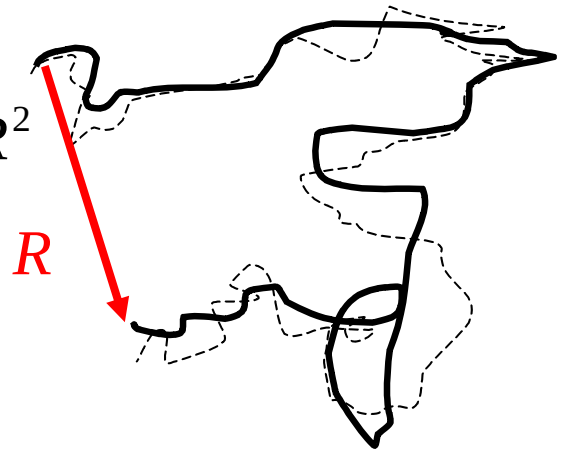


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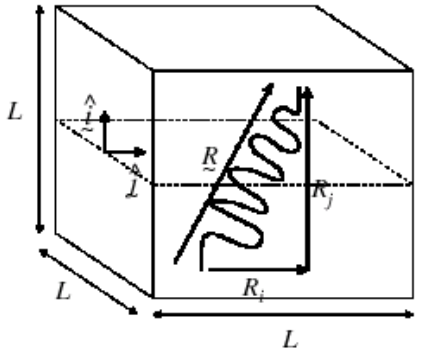


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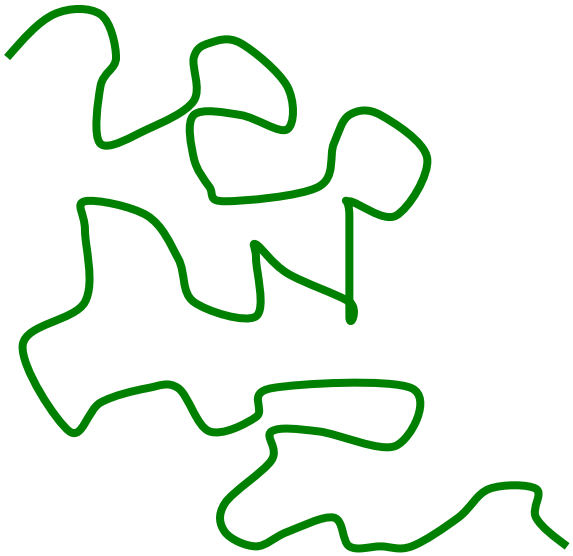
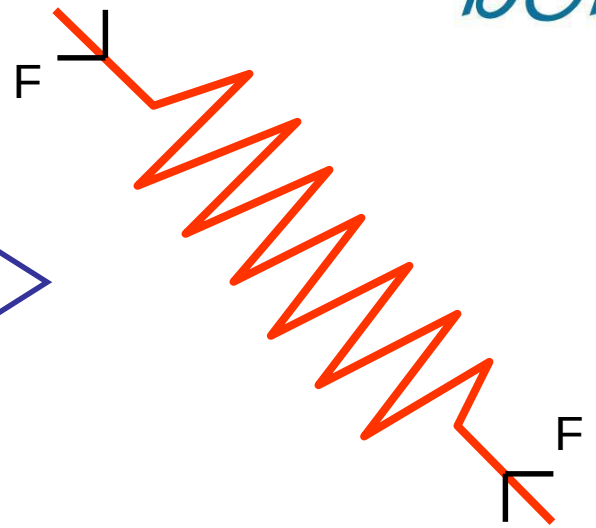
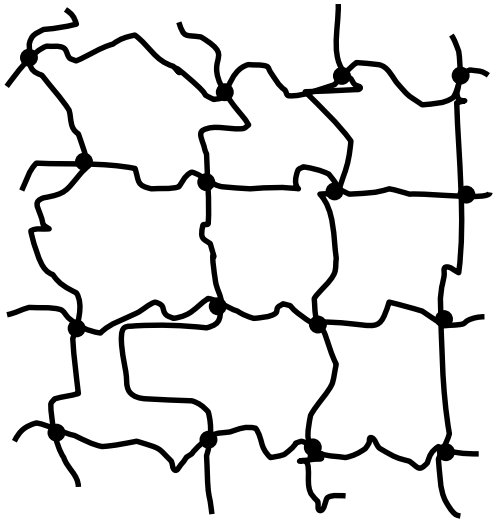


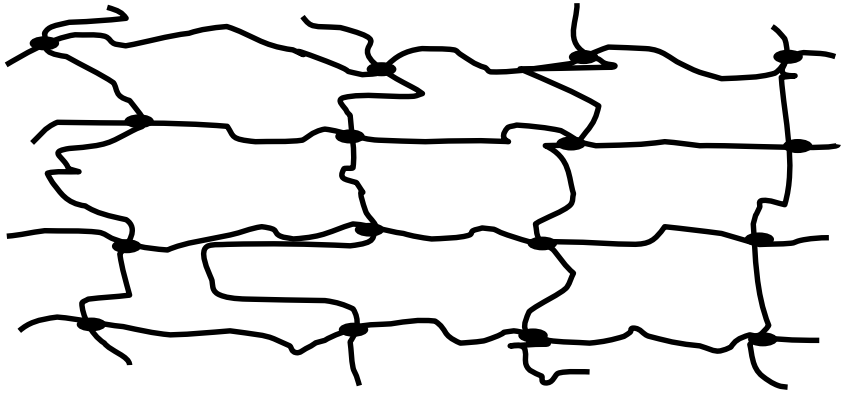



Long piece of string, in thermal motion

acts like a “thermal spring”

Rubber is a *crosslinked* polymer, and acts like lots of joined up springs.



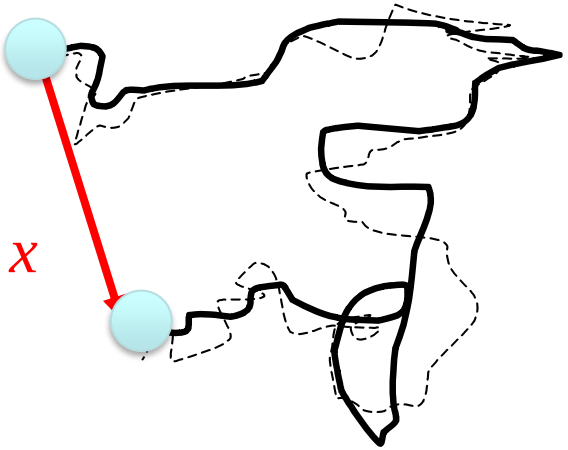


Gives a force when you stretch it!

# Diffusion and dissipation

For a particle diffusing with diffusion constant D, the mean square distance travelled in time t is:

$$\left\langle x^2 \right\rangle = 2Dt$$




The diffusion constant is related to the particle friction constant by the Einstein relation (also known as a case of the fluctuation-dissipation theorem):

$$D = \frac{k_B T}{\varsigma}$$

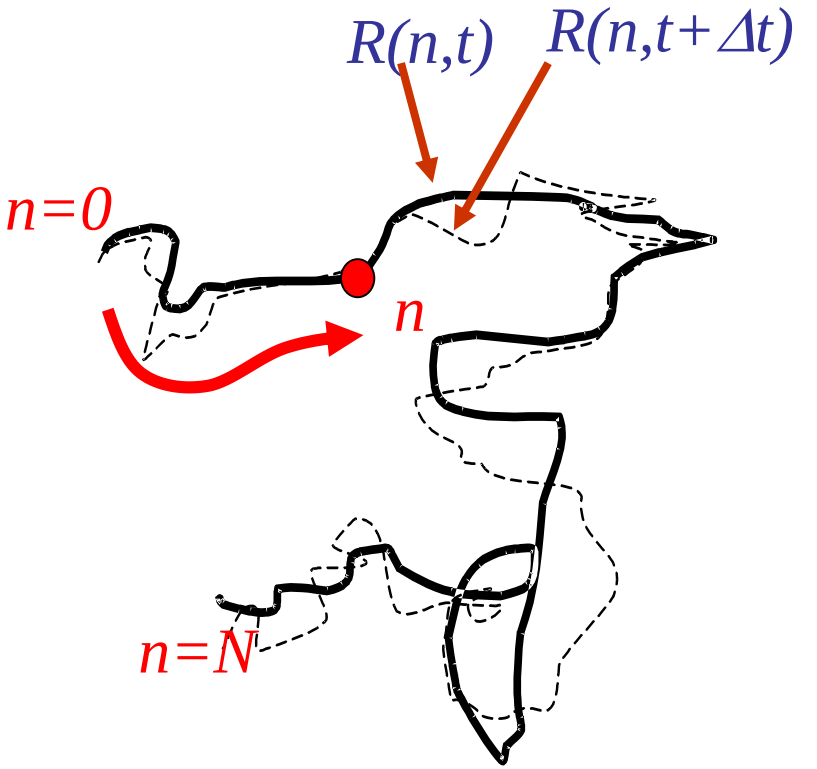
More detailed mathematical descriptions also exist, e.g. Langevin equations:

$$\varsigma \frac{dx}{dt} = F_{ext} + f \quad \text{where} \quad \left\langle f(t) f(t') \right\rangle = 2k_B T \varsigma \delta(t - t')$$

# The Rouse model

Polymer chains are in constant motion due to the thermal energy of their surroundings.

The Rouse model is the simplest model of this dynamics. It assumes chains are random walks, and that friction is local.




Relaxation time for *n* monomers:

$$D = \frac{D_{mon}}{n}$$

$$R^2 = nb^2$$

$$\tau(n) = \frac{R^2}{D} = \frac{n^2 b^2}{D_{mon}} = n^2 \tau_{mon}$$

Relaxation time for whole chain is the **Rouse time**:

$$\tau_R = \tau(N) = N^2 \tau_{mon}$$

Rouse relaxation is **hierarchical**. Groups of *n* monomers relax in time *t* so:

$$n(t) = \left(\frac{t}{\tau_{mon}}\right)^{1/2}; \quad R(t) = b\left(\frac{t}{\tau_{mon}}\right)^{1/4}$$

# The Rouse model - consequences

Relaxation time for whole chain is the **Rouse time** – this increases with the square of the molecular weight:

$$\tau_R = \tau(N) = N^2 \tau_{mon}$$

In linear rheology, modulus is **$k_B$T x no. of chains/volume**. So:

$$G = k_B T c_{chain} = \frac{k_B T c_{mon}}{N}$$

(i.e. the elastic modulus associated with the longest relaxation mode decreases with *N*).

So, the chain contribution to viscosity can be estimated as:

$$\mu = G\tau_R = \frac{k_B T c_{mon}}{N} N^2 \tau_{mon} = k_B T c_{mon} \tau_{mon} N$$

i.e. increasing in proportion to molecular weight.

For times earlier than the Rouse time, hierarchical relaxation gives:

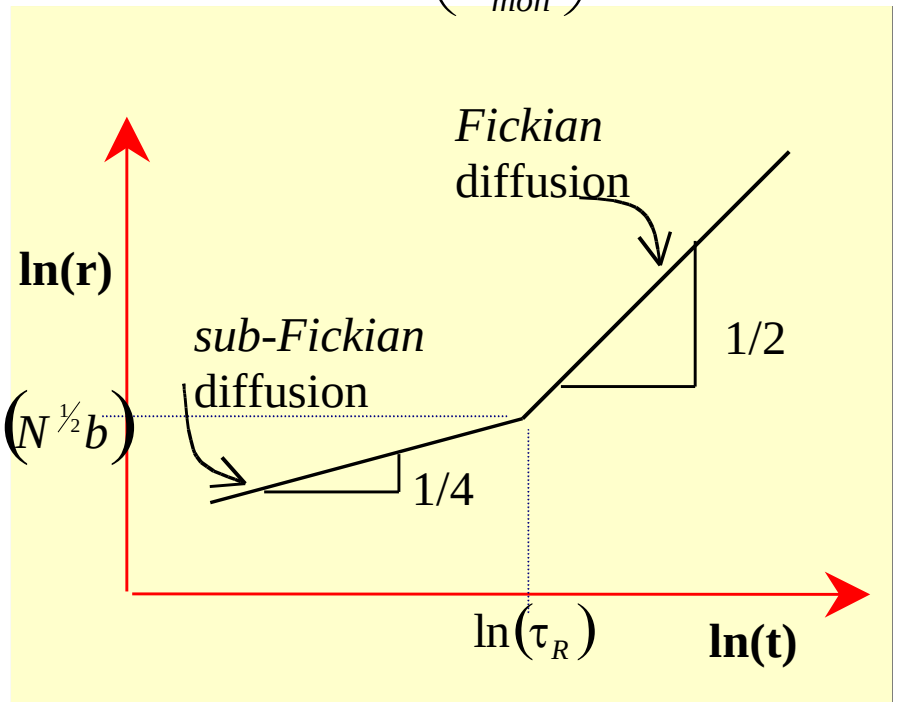
$$G(t) = \frac{k_B T c_{mon}}{n(t)} = k_B T c_{mon} \left( \frac{t}{\tau_{mon}} \right)^{-1/2}$$

# Consequences of hierarchical relaxation

Up until the Rouse time, internal sections of the chain are relaxing.

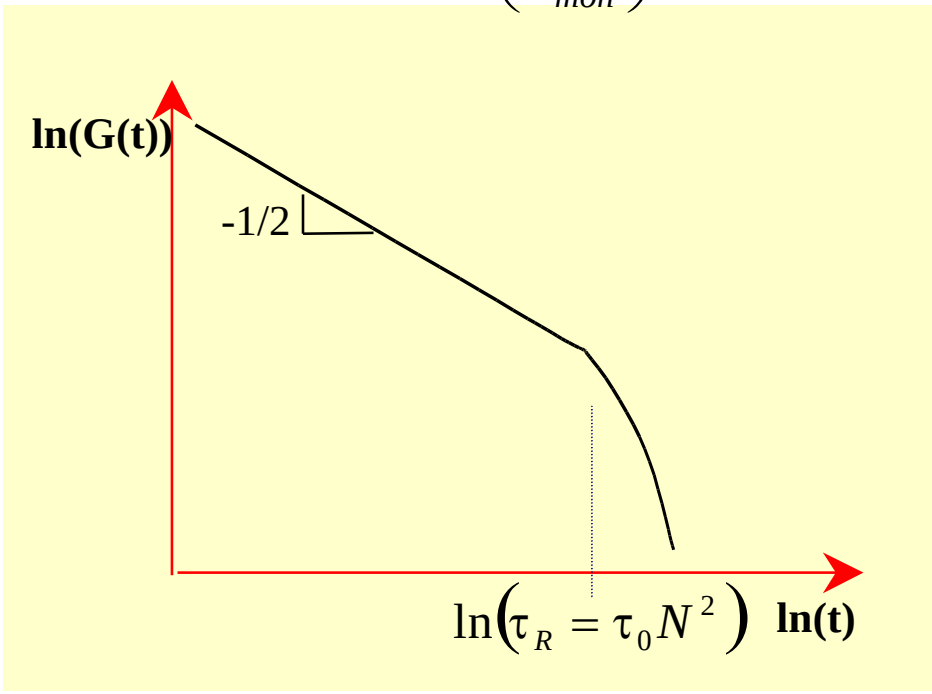
**Monomer diffusion:**

$$R(t) = b\left(\frac{t}{\tau_{mon}}\right)^{1/4}$$



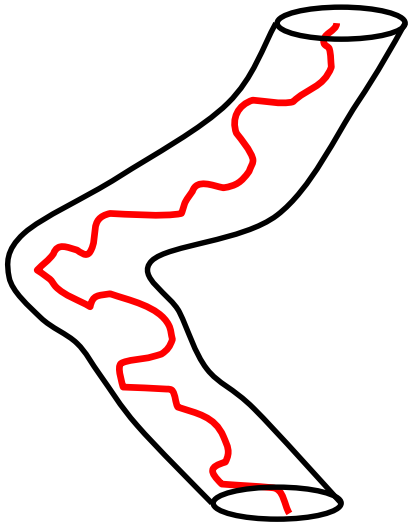

**Stress relaxation:**

$$G(t) = k_B T c_{mon}\left(\frac{t}{\tau_{mon}}\right)^{-1/2}$$




$$\tau_R = \tau(N) = N^2 \tau_{mon}$$

# Entangled Dynamics



Polymer chains are all tangled up – like spaghetti

Chains move by Brownian (thermal) motion, but;

They can only move along their own length

It's as though the polymers were trapped in a "tube"

Reduces a "many-chain" problem to a "single chain" problem

"Memory" time is how long it takes polymer to "wiggle" out of it's tube