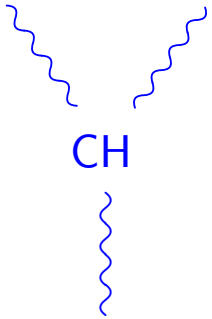
A microprimer on polymers

Polyethylene: . . .—CH_2—CH_2—CH_2—. . . or |—CH_2—$|_N$

Polystyrene: |—CH_2—CH—$|_N$

Typical lengths $N > 10^5$ possible, e.g., for polystyrene (REM: DNA has $N \lessapprox 10^9$)

Problems: polydispersity, branching



Polymer topologies: Linear, ring, brush, star, watermelon, dendrimers

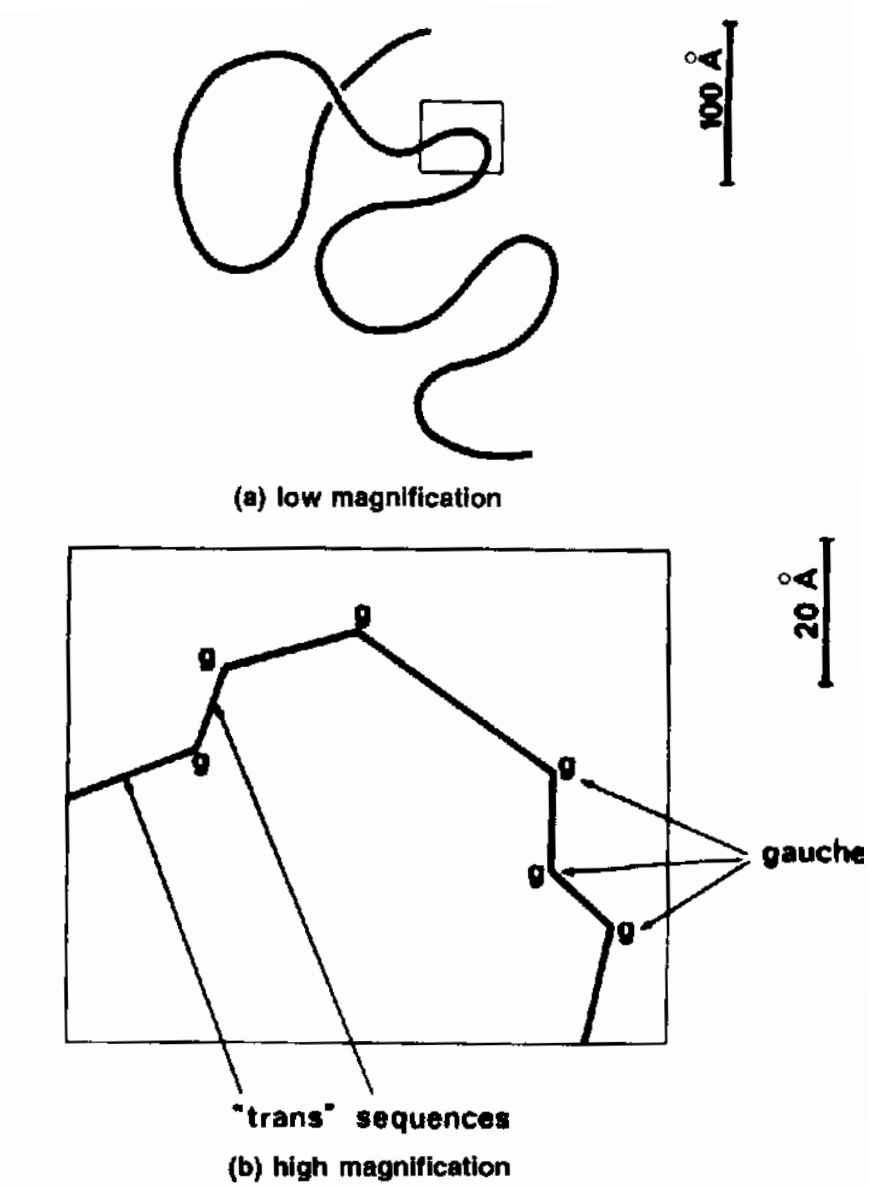

100 Å
(a) low magnification
20 Å
g
g
g
g
g
g
g
gauche
"trans" sequences
(b) high magnification

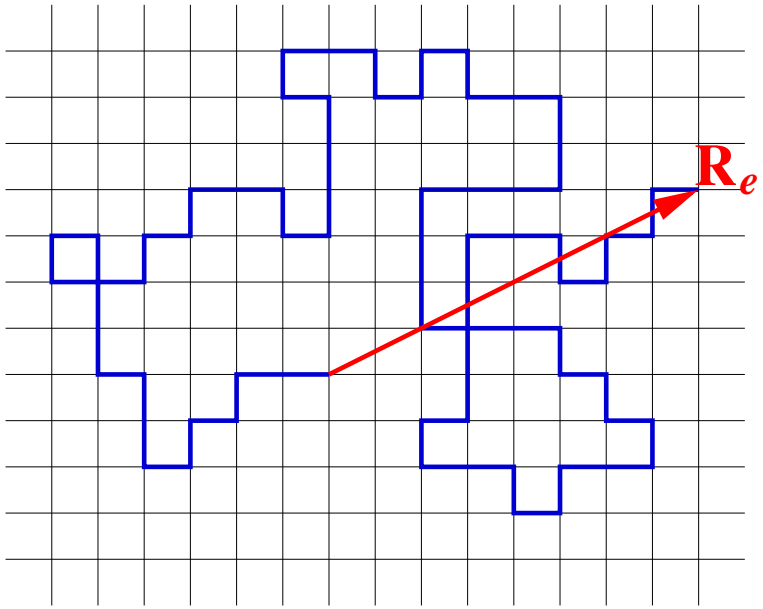
Figure 0.5.

Random walk model of polymers:

Periodic lattice with spacing a.

Each monomer has position $\mathbf{r}_i$, $i = 0, 1, 2, \ldots, N$.

Monomer-monomer vector: $\mathbf{a}_{i+1} = \mathbf{r}_{i+1} - \mathbf{r}_i$



End-to-end vector:

$$\mathbf{R}_e = \sum_i \mathbf{a}_i$$

Independent orientations of monomers:

$$\mathbf{R}_0^2 = \langle \mathbf{R}_e^2 \rangle = \sum_{i,j} \langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = \sum_i \langle \mathbf{a}_i^2 \rangle = N a^2.$$

$R_0 \simeq N^{1/2} a$ is a measure for the size of the random walk.

Centre of gravity:

$$\mathbf{R}_G = \frac{1}{1+N}\sum_{i=0}^{N}\mathbf{r}_i$$

Gyration radius:

$$R_g^2 = \frac{1}{1+N}\sum_{i=0}^{N}\langle(\mathbf{r}_i - \mathbf{R}_G)^2\rangle = \frac{1}{(1+N)^2}\sum_{i=0}^{N-1}\sum_{j=i+1}^{N}\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle$$

With $\mathbf{r}_j - \mathbf{r}_i = \sum_{n=i+1}^{j}\mathbf{a}_n$ one can show that $R_g^2 = a^2N(N+2)/[6(N+1)]$ such that for large N, $R_g \simeq a^2N/6$:

$$R_g \sim R_0 \sim aN^{1/2}.$$

REM: R_g is defined $\forall$ polymer topologies, in contrast to R_0 (the end-to-end vector is trivial for a ring . . .).

№ distinct walks with N steps: μ^N ($\mu = 2d$: connectivity constant)

№ distinct walks with N steps and end-to-end vector $\mathbf{r}$: $\mathcal{N}_N(\mathbf{r})$:

$$\sum_{\mathbf{r}} \mathcal{N}_N(\mathbf{r}) = \mu^N$$

PDF to find a walk with end-to-end vector $\mathbf{r}$:

$$p(\mathbf{r}) = \frac{\mathcal{N}_N(\mathbf{r})}{\sum_{\mathbf{r}} \mathcal{N}_N(\mathbf{r})}$$

For large N in continuum limit:

$$p(\mathbf{r}) = \left(\frac{d}{2\pi N a^2}\right)^{d/2} \exp\left(-\frac{d r^2}{2 N a^2}\right)$$

such that $\langle \mathbf{r}^2 \rangle = N a^2$

At fixed end-to-end distance the entropy of the random walk is:

$$S(\mathbf{r}) = S_0 - k_B \frac{dr^2}{2Na^2}$$

where S_0 absorbs all constants

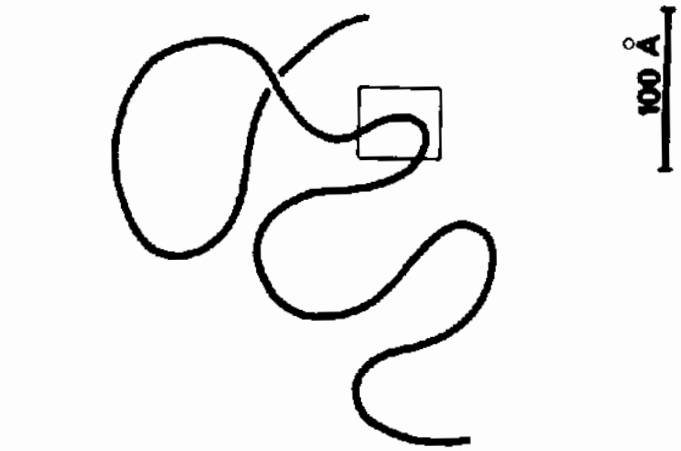
Free energy $\mathscr{F}(\mathbf{r}) = E - TS$ @ fixed $\mathbf{r}$:

$$\mathscr{F}(\mathbf{r}) = \mathscr{F}_0 + k_B T \frac{dr^2}{2Na^2}$$

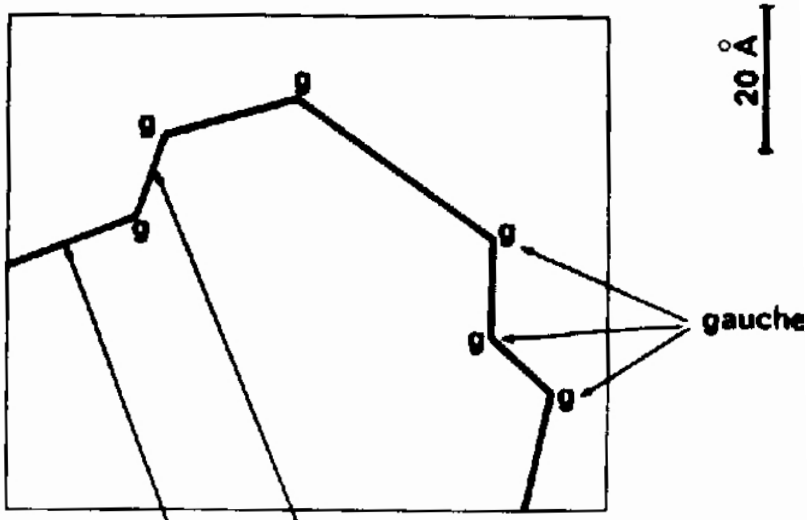
Restoring force:

$$\mathbf{F} = -\frac{dk_B T}{R_0^2}\mathbf{r}$$

Entropic elasticity, always Hookean



(a) low magnification



(b) high magnification

Figure 0.5.

Persistence length

$\Delta\epsilon > k_B T$: Rigid chain

$\Delta\epsilon \approx k_B T$: Locally rigid, flexible @ larger scales

Measure is persistence length:

$$\ell_p = \ell_0 \exp\left(\frac{\Delta\epsilon}{k_B T}\right)$$

Flexible behaviour at small x:

$$x = \frac{\ell_p}{L} \simeq N^{-1} \exp\left(\frac{\Delta\epsilon}{k_B T}\right)$$

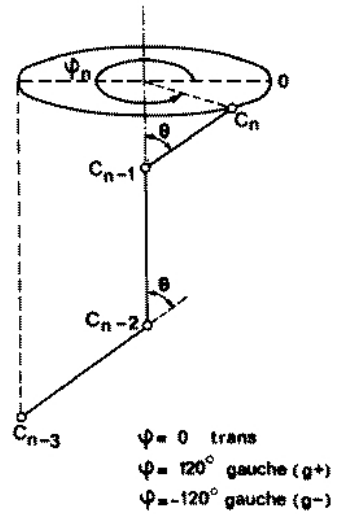


Figure 0.2.

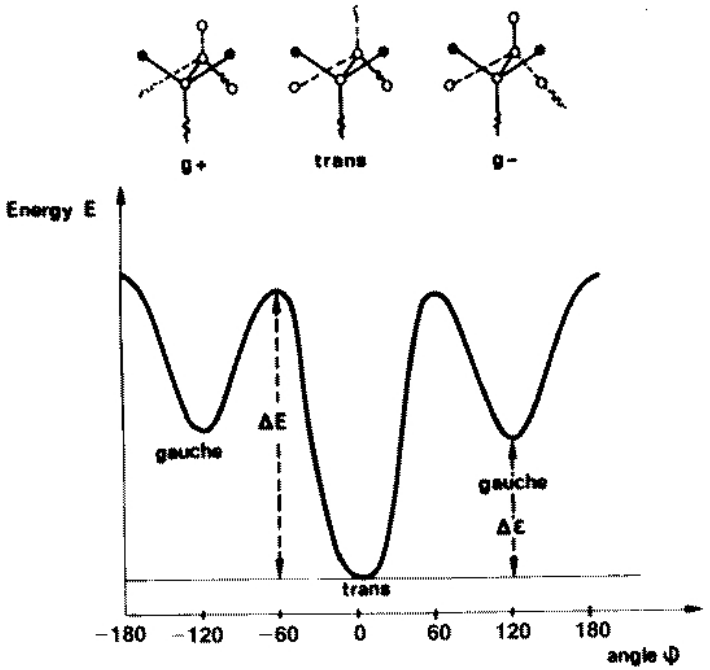


Figure 0.3.

Freely jointed and freely rotating chains

Freely jointed chain: end-to-end vector and squared end-to-end-distance:

$$\mathbf{R}_e = \sum_i \mathbf{a}_i, \qquad \mathbf{R}_0^2 = \langle \mathbf{R}_e^2 \rangle = \sum_{i,j} \langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = \sum_i \langle \mathbf{a}_i^2 \rangle = N a^2$$

Freely rotating chain à la Doi & Edwards:

$$\langle \mathbf{a_n} \rangle_{\mathbf{a}_m, \mathbf{a}_{m+1}, \ldots, \mathbf{a}_{n-1} \text{ fixed}} = \mathbf{a}_{n-1} \cos\theta$$

Multiplying by $\mathbf{a}_m$:

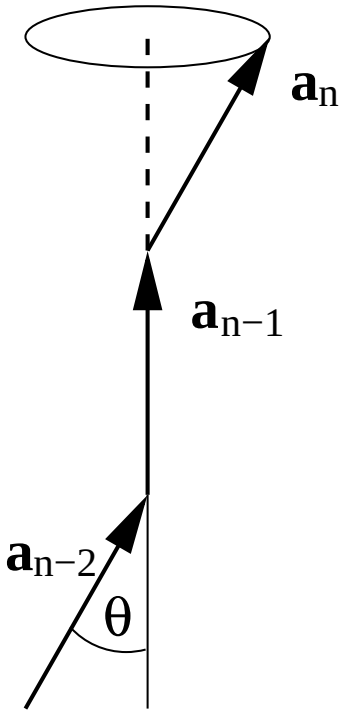
$$\langle \mathbf{a}_m \cdot \mathbf{a_n} \rangle_{\mathbf{a}_m, \mathbf{a}_{m+1}, \ldots, \mathbf{a}_{n-1} \text{ fixed}} = \mathbf{a}_m \cdot \mathbf{a}_{n-1} \cos\theta$$

Averaging over $\mathbf{a}_m, \ldots, \mathbf{a}_{n-1}$:

$$\langle \mathbf{a}_m \cdot \mathbf{a_n} \rangle = \langle \mathbf{a}_m \cdot \mathbf{a_{n-1}} \rangle \cos\theta$$

With initial condition $\langle \mathbf{a}^2 \rangle = a^2$, we find:

$$\langle \mathbf{a}_m \cdot \mathbf{a_n} \rangle = a^2 \cos^{|n-m|}\theta$$



Length scale

$$\ell_p = \frac{a}{\log\cos\theta}$$

$$\sum_{-\infty}^{\infty}\langle \mathbf{a}_{n+k}\cdot\mathbf{a}_n\rangle = a^2\left(1+2\sum_{k=1}^{\infty}\cos^k\theta\right) = a^2\frac{1+\cos\theta}{1-\cos\theta} \implies R_0^2 = a^2 N\frac{1+\cos\theta}{1-\cos\theta}$$

freely jointed chain with rescaled monomer length

Persistence lengths

Flexible rod:

$$\ell_p = \frac{\pi \mathsf{Y} \left(R^4 - R_i^4\right)}{4 k_B T} \;\therefore\; \text{Young's modulus } \mathsf{Y}$$

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Spaghetti $\varnothing = 2\text{mm}$, $\mathsf{Y} = 10^9 \text{erg/cm}^3$, $T = 300\text{K}$; $k_B = 1.38 \times 10^{-16}\text{erg/K}$:

$$\ell_p \approx 2 \times 10^{18}\text{cm} = 2 \times 10^{13}\text{km} \approx 2\text{ly}$$

or 1/2 distance to Proxima centauri

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Spaghetti of $\varnothing = 2\text{nm}$:

$$\ell_p \approx 20\text{nm}$$

Persistence lengths

Table 2.2. Linear density λ_p (mass per unit length) and persistence length ξ_p of some biologically important polymers.

Polymer	*Configuration*	λ_p (D/nm)	ξ_p (nm)
Long alkanes	linear polymer	~110	~0.5
Spectrin	2-strand filament	4,500	10-20
DNA	double helix	1,900	53 ± 2
F-actin	filament	16,000	$10\text{-}20 \times 10^3$
Intermediate filaments	32 strand filament	~35,000	
Tobacco mosaic virus		~140,000	$\sim 1 \times 10^6$
Microtubules	13 protofilaments	160,000	$1\text{-}6 \times 10^6$

Nonphantom chains, self-excluding volume à la Flory

Consider chain with radius R and internal monomer concentration $c_{\rm int} \simeq N/R^d \rightsquigarrow$ local repulsive energy:

$$\mathscr{F}_{\rm rep|loc} = \frac{1}{2} k_B T v(T) c_{\rm int}^2$$

Here, $v(T)$ is the excluded volume parameter:

$$v(T) = (1 - 2\chi) a^d$$

where under Θ condition $\chi = 1/2$ corresponds to an ideal chain

Total repulsive energy (mean field $\langle c^2 \rangle \longrightarrow \langle c \rangle^2 \sim c_{\rm int}^2$):

$$\mathscr{F}_{\rm rep|tot} \simeq k_B T v(T) c_{\rm int}^2 R^d = k_B T v(T) \frac{N^2}{R^d}$$

favouring large values of R (swelling)

Entropic contribution:

$$\mathscr{F}_{\rm el} \simeq k_B T \frac{R^2}{N a^2}$$

Total free energy:

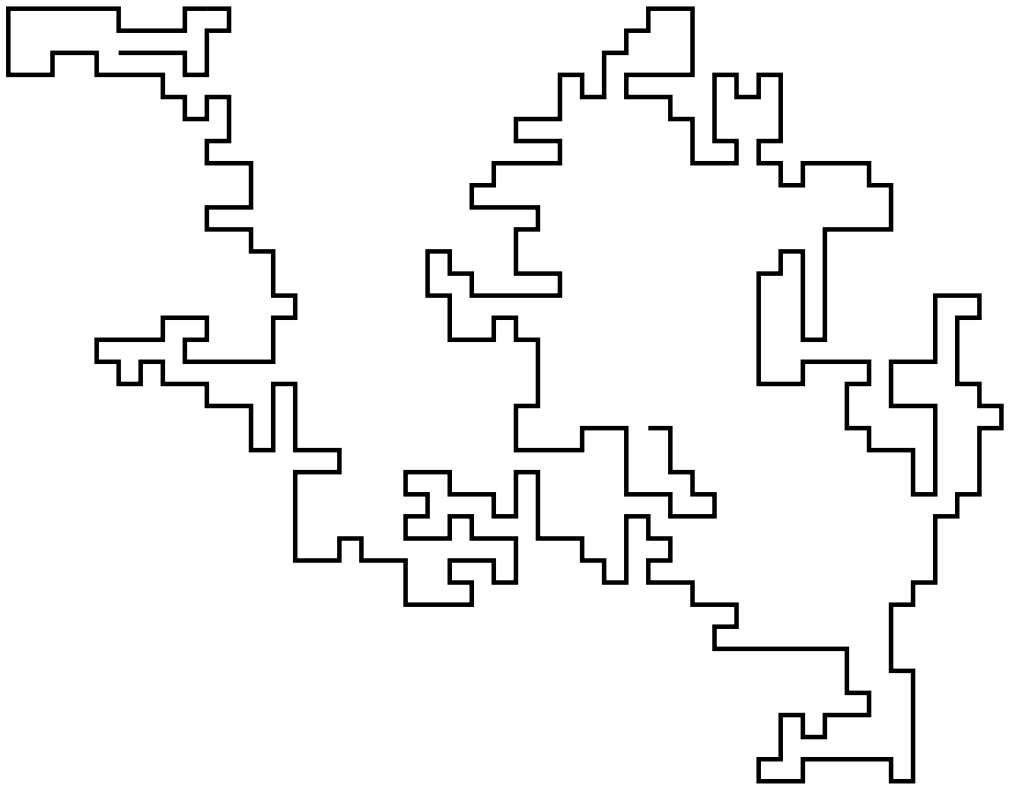
$$\mathscr{F} \simeq k_B T \left(v(T) \frac{N^2}{R^d} + \frac{R^2}{N a^2} \right)$$

Minimisation at Flory radius:

$$R_F = \left(v(T) a^2 N^3 \right)^{1/(2+d)} \simeq A N^{\nu} \;\; \therefore \;\; \nu = \frac{3}{2+d}$$

Dimension	Flory result	Best value
1	$\nu_F = 1$	$\nu_{\rm field} = 1$
2	$\nu_F = 0.75$	$\nu_{\rm field} = 0.75$
3	$\nu_F = 0.6$	$\nu_{\rm field} = 0.588$

Self-avoiding walk (SAW):



Effective connectivity constant:
$\mu_{\mathrm{SAW}} \neq \mu_{\mathrm{phantom}}$

Linear chain introduces the configuration exponent γ:

$$\omega \simeq \mu^N N^{\gamma-1}$$

Dimension	Connectivity constant	Configuration exponent
2	$\mu \in [2.62, 2.68]$	$\gamma \approx 1.33$
3	$\mu \in [4.57, 4.74]$	$\gamma \approx 1.16$