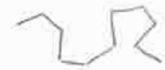
- FJC : freely jointed chain



N links of length b.

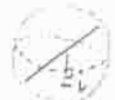
- Thermodynamics T, V, N

free energy $A = U - TS$ => want to maximize S : purely entropic reasoning

U → * zero contribution; T → fixed

* $U = 0$ for all configurations (assumption) : no penalty for {bending, crossing...
all configurations are equally likely

- Single link point of view



$\underline{b}_i$ = orientation of link i
maximize entropy with all orientations equally likely

- Sample configuration (microstate)

$\underline{R}$ = end-to-end vector = "measure of coil size"

- Statistics of a random flight (walk) :

$$\underline{R} = \sum_{i=1}^{N} \underline{b}_i$$

mean $\langle \underline{R} \rangle = \langle \sum_{i=1}^{N} \underline{b}_i \rangle = \sum_{i=1}^{N} \langle \underline{b}_i \rangle = \underline{0}$

variance $\langle \underline{R} \cdot \underline{R} \rangle = \left\langle \left(\sum_{i=1}^{N} \underline{b}_i \right) \cdot \left(\sum_{j=1}^{N} \underline{b}_j \right) \right\rangle = \langle \sum_{i=1}^{N} \underline{b}_i \cdot \underline{b}_i \rangle = \sum_{i=1}^{N} \langle \underline{b}_i \cdot \underline{b}_i \rangle = N \langle b^2 \rangle = Nb^2$

↳ orientations uncorrelated unless $i = j$

$$\boxed{\sqrt{\langle \underline{R} \cdot \underline{R} \rangle} = \sqrt{\langle R^2 \rangle} = \sqrt{N}\, b}$$

measure of the size (extension) of polymer

Contour length of chain $= Nb$ => on average, molecule much shorter than its contour length : at equilibrium, polymers are coiled

- Probability distribution for $\underline{R}$

$$p(x, y, z, N) \approx \left(\frac{3}{2\pi N b^2} \right)^{-3/2} \exp\left(\frac{-3R^2}{2Nb^2} \right)$$

Gaussian $\mu = |\langle \underline{R} \rangle| = 0$, $\sigma^2 = \frac{Nb^2}{3}$

probability that chain end is in volume $\begin{pmatrix} x \to x + dx \\ y \to y + dy \\ z \to z + dz \end{pmatrix} = p(x, y, z, N)\, dx\, dy\, dz$

similar to diffusion process

- Limits of validity : calculate correction term

$$p(\underline{R}, N) = p_{Gaussian} \left[1 - \frac{3}{20N} \left(5 - \frac{10R^2}{Nb^2} + \frac{3R^4}{N^2 b^4} \right) \right]$$

Gaussian if
* $N \gg 1$ many links
* $R^2 \ll N^2 b^2$ not valid for large extensions $R \to L = Nb$
$R^2 \ll L^2$

- Force - extension behavior of a single molecule
- Let's constrain our system to fixed $\underline{R}$; { force $\underline{f}$ allowed to vary, extension is fixed

probability of random walk $p(\underline{R}) = \dfrac{\Omega(\underline{R})}{\Omega_{total}}$ ← number of configurations with $\underline{R}$
← total number of configurations for molecule

number of configurations with end-to-end vector $\underline{R}$: $\boxed{\Omega(\underline{R}) = p(\underline{R})\ \Omega_{total}}$
↳ not function $\underline{R}$!

- forces & thermodynamics

from 02/12/2003 , $dA = -PdV + \underline{f}\ d\underline{R} - SdT$

$$\langle \underline{f} \rangle = \left(\frac{\partial A}{\partial \underline{R}}\right)_{V,T}$$ relationship between force & free energy

here $A = U - TS = -TS$; hence $\boxed{\langle \underline{f} \rangle = -T\left(\dfrac{\partial S}{\partial \underline{R}}\right)_{T,V}}$

constrained system $S = k \ln \Omega(\underline{R})$

$$S = \underbrace{k \ln \Omega_{total}}_{} + k \ln p(\underline{R})$$

not a function of $\underline{R}$ ⟹ will fall off in differentiation with respect to $\underline{R}$

$$\langle \underline{f} \rangle = -kT \frac{\partial}{\partial \underline{R}}\left(\ln p(\underline{R})\right) = \frac{3kT}{Nb^2}\underline{R}$$ from Gaussian expression of $p(\underline{R})$

$$\boxed{\langle \underline{f}^{Gaussian} \rangle = \underbrace{\frac{3kT}{b}}_{} \cdot \frac{\underline{R}}{L}}$$ linear relationship between $\underline{f}$ and $\underline{R}$

energy / length ≡ force , hence $\frac{kT}{b}$ is the characteristic force to extend chain
b : measure of rigidity

- valid for $N \gg 1$, $R \ll L$

$\frac{kT}{b}$ determines how difficult it is to extend polymer

"stiffer" molecules (larger b) are easier to extend ($N = \frac{L}{b}$ less segments, less configurations)

entropic elasticity

the form for $\langle \underline{f}^{Gaussian} \rangle$ allows for $R > L$ (unphysical)

▷ ds DNA double stranded DNA

Kuhn length $b \simeq 100$ nm

recall $\dfrac{kT}{1\,nm} \simeq 4$ pN ⟹ $\dfrac{kT}{100\,nm} \simeq 0.04$ pN

$$\langle \underline{f}^{DNA} \rangle \simeq 0.12 \text{ pN} \cdot \frac{\underline{R}}{L}$$

- see overhead for arbitrary force (you fix force rather than extension)

by getting Q', you can express $\langle \underline{r} \rangle$ as a function of $\underline{f}$.

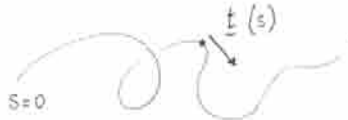
$$\langle \underline{r} \rangle = \underbrace{Nb}_{\text{length}} \underbrace{\left[\coth\left(\frac{fb}{kT}\right) - \frac{kT}{fb}\right]}_{\text{Langevin } \mathcal{L}\left(\frac{fb}{kT}\right)} \underbrace{\frac{\underline{f}}{f}}_{\text{vector}}$$ no approximation (if $fb \ll kT$ back to Gaussian)

- check on Current Opinion [...] plot that approximates fairly well the force / extension behavior of ds DNA

but not as well as the next model ... WLC

□ WLC · worm-like chain

- Continuous, thin, flexible rod, constant contour length



s = arc length
$\underline{t}(s)$ = unit tangent at s

- Bending energy (from continuum mechanics)

R_c = radius of curvature

$$\frac{E_{arc}}{L_{arc}} = \frac{\kappa_f}{2R_c^2} = \frac{YI}{2R_c^2}$$

κ_f : flexural rigidity
Y : Young's modulus
I : second moment of inertia $\quad \left\{ I = \int x^2 \, dA \right.$
E_{arc} : arc energy $\quad x$ = distance from center of cross-section

continuous model : $\frac{E_{arc}}{L_{arc}} = \frac{\kappa_f}{2}\left(\frac{\partial t}{\partial s}\right)^2$

total internal energy $\boxed{U = \frac{\kappa_f}{2}\int_0^L \left(\frac{\partial t}{\partial s}\right)^2 ds}$

- Some properties of the worm-like chain model
  - equilibrium (no force)

    $\langle \underline{t}(s) \cdot \underline{t}(s+\Delta s) \rangle = \exp\left(\frac{-\Delta s \, kT}{\kappa_f}\right)$ $\left\{ \begin{array}{l} \text{exponential decay} \\ \text{no correlation when } \Delta s \to +\infty \end{array} \right.$

    $\frac{\kappa_f}{kT}$ is a length . persistence length $\boxed{l_p = \frac{\kappa_f}{kT}}$

  - coil size

    $$\langle R^2 \rangle = 2\, l_p \left[\frac{L}{l_p} + \exp\left(\frac{-L}{l_p}\right) - 1 \right]$$

    two regimes * $l_p \gg L$
    rigid $\Rightarrow \langle R^2 \rangle \to L^2$
    * $l_p \ll L$
    flexible $\Rightarrow \langle R^2 \rangle \to 2\, l_p L$
    recall FJC $\langle R^2 \rangle_{FJC} = b L$ $\quad \boxed{l_p = \frac{b}{2}}$ conversion between WLC & FJC