

# ENAS 606 : Polymer Physics

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## Ideal Chain Statistics, Free Energy and Chain Deformation

### 1 Probability Distribution of End-End Distances

We develop expressions for the probability distribution of end-end distances of a polymer chain. We start from a simple random walk in one dimension, and generalize the result to three dimensions.

In one dimension, the number of ways of arriving a distance  $x$  from the origin after  $N$  steps of unit size ( $n_+$  in the positive direction and  $n_-$  in the negative) is given by a combinatorial expression.

$$W(N, x) = \frac{N!}{(n_+!)(n_-!)} \quad (1)$$

where  $x = n_+ - n_-$ ,  $N = n_+ + n_-$  and so  $n_+ = (N + x)/2$ , and  $n_- = (N - x)/2$ . The probability of this occurrence is just the number of ways of realizing the occurrence divided by the total number of possible trajectories.

$$p(N, x) = \frac{1}{2^N} \frac{N!}{(n_+!)(n_-!)} \quad (2)$$

We consider the natural logarithm of the above probability. Using Stirling's approximation,  $N! \cong \sqrt{2\pi N}(N/e)^N$ , and assuming that  $x \ll N$  we arrive at the probability distribution function, which is the probability  $p(N, x)dx$  that the trajectory of the random walk is terminated within an interval  $dx$  from  $x$ .

$$\begin{aligned} P(N, x) &= \frac{1}{\sqrt{2\pi N}} \exp\left(\frac{-x^2}{2N}\right) \\ \langle x^2 \rangle &= \int_{-\infty}^{\infty} x^2 P(N, x) dx = N \\ P(N, x) &= \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} \exp\left(\frac{-x^2}{2\langle x^2 \rangle}\right) \end{aligned} \quad (3)$$

In three dimensions, the probability  $P(N, R)$  is just the product of  $P(N, R_x)P(N, R_y)P(N, R_z)dx dy dz$  and since  $\langle R^2 \rangle = Nb^2$ ,

$$P(N, R) = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} \exp\left(\frac{-3R^2}{2Nb^2}\right) \quad (4)$$

so the probability of finding the chain end (terminus of an ideal random walk) in a spherical shell between  $R$  and  $R + dR$  is  $P(N, R) 4\pi R^2 dR$ .

## 2 Entropic Free Energy of a Polymer Chain

The free energy of an ideal polymer chain is derived from its conformational entropy, described by the probability distribution above. The entropy as a function of the end to end distance  $R$  is provided by Boltzmann's relation  $S = k \ln \Omega(R)$  where  $\Omega(R)$  is simply the number of ways (conformations) of arranging monomers such that the chain has an end-end distance  $R$ . The free energy is given below.

$$S(N, R) = \frac{-3}{2} k \frac{R^2}{Nb^2} + S_0 \quad (5)$$

$$F(N, R) = \frac{3}{2} kT \frac{R^2}{Nb^2} + F_0 \quad (6)$$

The expressions above in Equation 6 relate the free energy of the polymer chain very simply to a ratio between the end-end distance  $R$  and the unperturbed end-end distance,  $Nb^2$ . The force required to perturb the chain dimensions is just given by

$$f = \frac{\partial F}{\partial R} = \frac{3kT}{Nb^2} R \quad (7)$$

This expression is linear in the displacement  $R$  and scales directly with temperature  $T$ . i.e. the polymer acts as an entropic spring, and becomes stiffer with increasing temperature. The above expression only holds true for deformations which do not significantly perturb the chain conformation, i.e. which do not make the chain conformation depart from Gaussian statistics. It is valid only in the limit where the deformation is small compared to the contour length of the polymer chain.

For a worm-like polymer chain, an approximate expression is provided by Siggia *et al.* [4], that fits small and large extensions

$$f = \frac{kT}{b} \left[ \frac{2\langle R \rangle}{R_{max}} + \frac{1}{2} \left( \frac{R_{max}}{R_{max} - \langle R \rangle} \right)^2 - \frac{1}{2} \right]$$

## 3 Blobs: Crossover length scales

An important concept in the treatment of perturbations to polymer chain structure is that of a *blob* [5]. It describes a length scale below which the polymer chain may be considered to be unperturbed by other forces or effects, whether they are excluded volume effects, surface interactions or external forces of tension or compression. Since the entire chain is in a thermal bath, on some length scale, thermal energy becomes the overriding influence and thus at length scales below this, the polymer exhibits ideal behavior.

We divide the polymer chain into blobs of size  $\xi$ , with  $g$  monomers per blob. The size of the blob is described by ideal chain statistics, so  $\xi \approx bg^{1/2}$ .

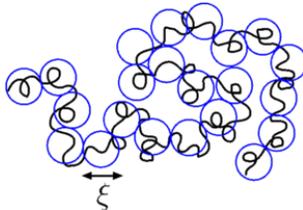


Figure 1: The polymer chain can be thought of as being composed of blobs within which the chain executes an unperturbed random walk, i.e. obeys Gaussian statistics

### 3.1 Polymer Chain in Tension

For example, in elongation of a polymer chain due to tension, we may assume these blobs are more or less lined-up along the direction of deformation. The number of blobs is  $(N/g)$  so that the extension  $R \approx \xi(N/g)$ . From this, we see that

$$\begin{aligned}\xi &\approx Nb^2/R \\ g &\approx N^2b^2/R^2\end{aligned}\tag{8}$$

The free energy of the chain is increased in tension due to the restriction of the degrees of freedom of the blobs - each blob in this case contributes  $kT$  and so

$$F \approx kT N/g \approx kT \frac{R^2}{Nb^2}$$

If we consider the force required to stretch the polymer coil

$$f = \frac{\partial F}{\partial R} \approx kT \frac{R}{Nb^2} \approx kT/\xi\tag{9}$$

we see that the blob defines a length scale over which the elastic energy is  $\approx kT$ . That is, under an external force, the polymer will be unperturbed on length scales smaller than that for which the corresponding ‘thermal forces’ are  $kT$  or larger.

### 3.2 Pore Confinement - Chain in Biaxial compression

Confinement to a pore of diameter  $D$  sets the length scale of the blob, in the sense that on smaller length scales than  $D$ , the monomers or segments do not feel the confinement, and may execute an unperturbed random walk. We write equations for the size of the pore in terms of the number of segments in the blob, and then estimate the length that the polymer occupies in the tube,  $L$ , as that resulting from a random walk of the blobs in the tube.

$$\begin{aligned}D &\approx bg^{1/2} \\ L &\approx D(N/g)^{1/2} \approx bN^{1/2}\end{aligned}$$

The energetic penalty due to confinement is again  $kT$  per blob, so

$$F_{conf} \approx kT(N/g) \approx kTN(b/D)^2 \approx kT(R_0/D)^2\tag{10}$$

### 3.3 Slit Confinement - Chain in Uniaxial Confinement

The blob length scale is set by the size of the slit,  $D$ . The polymer chain executes a random walk within the slit, with a radius (2-dimensional) given by

$$\approx D(N/g)^{1/2} \approx bN^{1/2}\tag{11}$$

That is, the result is as above. We will see later that for real chains which make a self-avoiding random walk/possess excluded volume interactions, this will not be the case.

### 3.4 Self Confinement due to Adsorption

A favorable energetic interaction with a surface will lead to confinement of the chain to lie within a distance  $\xi$  of the surface, which defines the blob length scale. We can make a very simple analysis which neglects entropic considerations, and describe the blob scale as that beyond which the interaction energy is larger than thermal energy. We require an expression for the number of monomer segments in each blob that are in contact with the surface. If we make a mean field assumption for the density of monomer segments in the blob, then the number of contacts is just this number density multiplied by the volume that exists within  $b$  of the surface, i.e.  $b\xi^2$ .

The volume fraction of segments in the blob is given by  $\phi \approx (b^3g/\xi^3) \approx b/\xi$  since  $\xi \approx gb^{1/2}$ . The number density of monomers in the blob is  $\phi/b^3$  and so the number of monomers in contact with the surface is

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

If the interaction energy with the surface is  $-\delta kT$  per monomer, then the energy gain per blob is simply

$$\delta kT\xi/b$$

which is approximately  $kT$  at the length scale  $\xi$ . This provides the size of the blob

$$\xi \approx b/\delta$$

Since each adsorption blob is of a size that it contributes  $kT$  to the energy, the chain energy is

$$F \approx -kT(N/g) \approx -kTN\delta^2 \tag{12}$$

## References

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