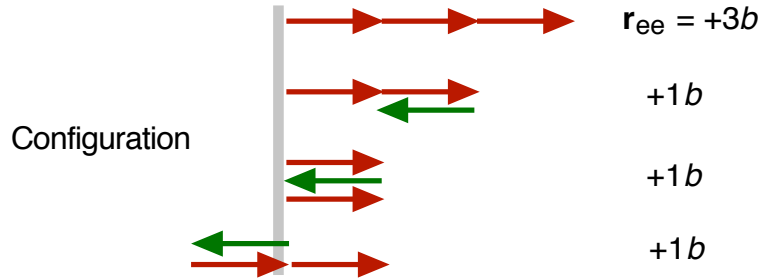


PHYS 4xx Poly 3 - Chain elasticity

Random chains in one dimension

Consider one-dimensional random chains with three segments: each link can point to the right or the left ($2^3 = 8$ possible configurations)



$C(r_{ee})$ = the number of configs with a given end-to-end displacement r_{ee} :

$$C(+3b) = 1 \quad C(+1b) = 3 \quad C(-1b) = 3 \quad C(-3b) = 1. \tag{1}$$

$C(r_{ee})$ equals the binomial coefficients in

$$(p + q)^3 = p^3 + (ppq + pqp + qpp) + (pqq + qpq + qqp) + q^3.$$

as the number of steps N increases, the distribution looks ever more Gaussian, and the general form for probability density is

$$P(x) = (2\pi\sigma^2)^{-1/2} \exp[-(x-\mu)^2 / 2\sigma^2] \quad (\text{normalized}) \tag{2}$$

$P(x) dx$ = probability of finding the observable x between x and $x + dx$

mean value = $\mu = \langle x \rangle = \int x P(x) dx \quad -\infty \leq x \leq +\infty$ (3)

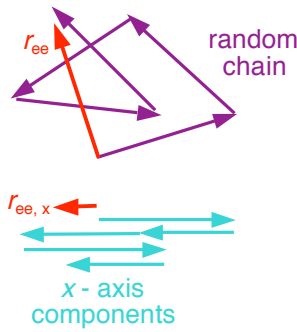
variance = $\sigma^2 = \langle (x - \mu)^2 \rangle = \langle x^2 \rangle - \mu^2$ (4)

random chains in one dimension obey $\langle x \rangle = 0$ and $\langle x^2 \rangle = Nb^2$

----> $\mu = 0$ and $\sigma^2 = Nb^2$ (one dimension) (5)

Random chain in three dimensions

By projecting their configurations onto a set of Cartesian axes, three-dimensional random chains can be treated as three separate one-dimensional systems



$$P(r_{ee,x}) = (2\pi\sigma^2)^{-1/2} \exp(-r_{ee,x}^2/2\sigma^2) \quad \text{with } \sigma^2 = N\langle b_x^2 \rangle \quad (6)$$

$\langle b_x^2 \rangle$ refers to the projection of the individual steps on the x-axis, which are independent of direction

$$\langle b_x^2 \rangle + \langle b_y^2 \rangle + \langle b_z^2 \rangle = \langle b^2 \rangle = b^2$$

implying

$$\langle b_x^2 \rangle = \langle b_y^2 \rangle = \langle b_z^2 \rangle = b^2/3, \quad (7)$$

hence:

$$\sigma^2 = Nb^2/3 \quad (\text{for three dimensions}). \quad (8)$$

Probability density (now per unit volume) at a given (x, y, z) is

$$P(x,y,z) = P(x)P(y)P(z) = (2\pi\sigma^2)^{-3/2} \exp[-(x^2+y^2+z^2)/2\sigma^2], \quad (9)$$

where $\sigma^2 = Nb^2/3$

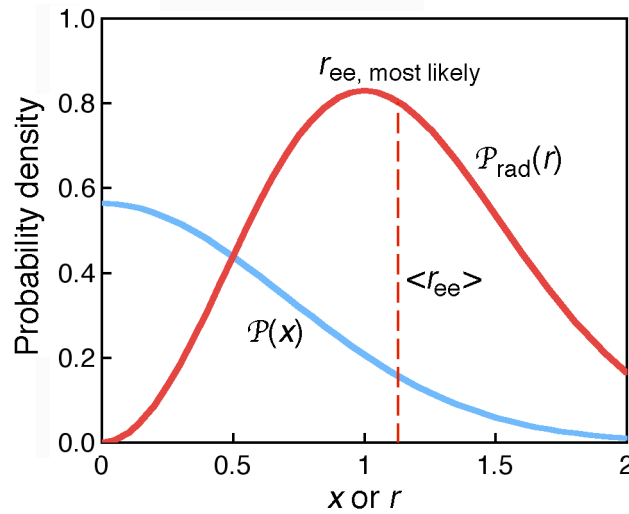
Eq. (9) says that the most likely set of coordinates for the tip of the chain is $(0,0,0)$; it does *not* say that the most likely value of r_{ee} is zero

The probability for the chain having a radial end-to-end distance between r and $r + dr$ is $P_{rad}(r)dr$ and can be obtained from

$$P(x,y,z)dx dy dz = P_{rad}(r)dr \quad (10)$$

so that

$$P_{rad}(r) = 4\pi r^2 (2\pi\sigma^2)^{-3/2} \exp(-r^2/2\sigma^2). \quad (11)$$



Summary of results for ideal chains in three dimensions

$$r_{ee, \text{ most likely}} = (2/3)^{1/2} N^{1/2} b \tag{12}$$

$$\langle r_{ee} \rangle = (8/3\pi)^{1/2} N^{1/2} b \tag{13}$$

$$\langle r_{ee}^2 \rangle = Nb^2. \tag{14}$$

Entropic elasticity

Eqs. (12) and (14) show that the largest number of chain configs occur near $r_{ee} = N^{1/2}b$. But entropy $S \sim \log(\text{configs.}) \rightarrow S$ of a chain must decrease as the chain is stretched. Since the configurations of freely-jointed chains have energy $E = 0$, then $F = E - TS \rightarrow F = -TS$

Conclusion: F increases as the chain is stretched because S decreases; hence, the chain resists stretching.

The elastic constant for entropic elasticity can be obtained through a comparison with the potential energy $V(x) = k_{sp}x^2/2$ for a Hookean spring. The argument goes as follows:

For a Hookean spring, at $T > 0$ the probability distribution $\mathcal{P}(x)$ for a displacement x goes like $\sim \exp(-E / k_B T)$
 $\rightarrow \mathcal{P}(x) \sim \exp(-k_{sp}x^2/2k_B T).$ (15)

Compare (15) with an ideal chain (6), $\mathcal{P}(x) \sim \exp(-x^2/2\sigma^2)$, to obtain

$$k_{sp} = k_B T / \sigma^2 \quad \text{with } \sigma^2 = Nb^2/d. \quad (\text{chains in } d \text{ dimensions})$$

Hence

$$k_{sp} = 3k_B T / Nb^2 = 3k_B T / 2\xi_{sp}L_c \quad (\text{three dimensions}) \tag{16}$$

where we have used $L_c = Nb$ and $\xi_p = b/2$ for an ideal chain.

Note: k_{sp} increases with temperature (for ideal chains, $\langle r_{ee}^2 \rangle = \text{constant}$, but $k_{sp} \sim T^1$)
 DEMO with weight hung from an elastic band

Highly stretched chains

Eq. (16) predicts that the force f required to produce an extension x is

$$f = (3k_B T / 2\xi_p L_c) x$$

or

$$x/L_c = (2\xi_p / 3k_B T) f. \quad (17)$$

Eq. (17) says that any x can be achieved with enough force; however, a chain with inextensible elements should not exceed $x/L_c = 1$.

Kuhn and Gr \ddot{u} n, 1942; James and Guth, 1943 (see also Flory, 1953, p. 427) have shown that a chain of rigid rods obeys

$$x/L_c = \mathcal{L}(2\xi_p f / k_B T), \quad (18)$$

where $\mathcal{L}(y)$ is the Langevin function

$$\mathcal{L}(y) = \coth(y) - 1/y. \quad (19)$$

Eq. (18) is better than the Gaussian approximation, but still not completely accurate for flexible filaments.

The worm-like chain (WLC) is based on Kratky-Porod model; its force-extension relationship is numerical but can be fitted by (Marko and Siggia, 1995):

$$\xi_p f / k_B T = (1/4)(1 - x/L_c)^{-1/2} - 1/4 + x/L_c. \quad (20)$$

Eqs. (18) and (20) are similar at large and small x but may disagree by up to 15% at intermediate forces.