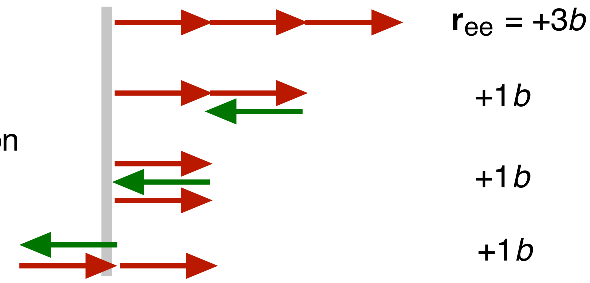
PHYS 4xx Poly 3 - Chain elasticity

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)



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

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

$C(\mathbf{r}_{ee})$ 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

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

$\mathcal{P}(x)\, dx$ = probability of finding the observable x between x and $x + dx$

mean value $= \mu = \langle x \rangle = \int x\, \mathcal{P}(x)\, dx \qquad -\infty \leq x \leq +\infty$ (3)

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

random chains in one dimension obey $\langle \mathbf{x} \rangle = 0$ 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

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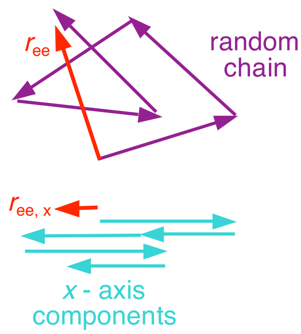

$$\mathcal{P}(r_{ee,x}) = (2\pi\sigma^2)^{-1/2} \exp(-r_{ee,x}^2/2\sigma^2) \quad \text{with } \sigma^2 = N\langle b_x^2\rangle \tag{6}$$

$\langle b_x^2\rangle$ 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

$$\langle b_x^2\rangle = \langle b_y^2\rangle = \langle b_x^2\rangle = b^2/3, \tag{7}$$

hence:

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

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

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

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 $\mathcal{P}_{rad}(r)dr$ and can be obtained from

$$\mathcal{P}(x,y,z)dx\,dy\,dz = \mathcal{P}_{rad}(r)dr \tag{10}$$

so that

$$\mathcal{P}_{rad}(r) = 4\pi r^2 (2\pi\sigma^2)^{-3/2} \exp(-r^2/2\sigma^2). \tag{11}$$

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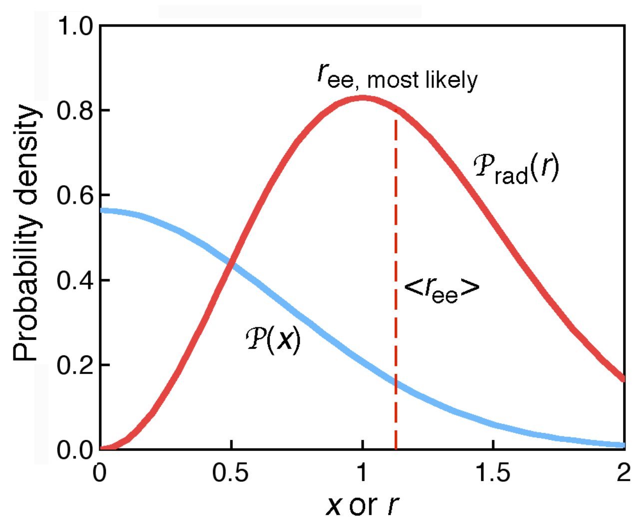

Summary of results for ideal chains in three dimensions

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

$<r_{ee}> = (8/3\pi)^{1/2}\ N^{1/2}\ b$ (13)

$<\mathbf{r}_{ee}^{\ 2}> = Nb^2$. (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(configs.) ---> S of a chain must decrease as the chain is stretched. Since the configurations of freely-jointed chains have energy $E = 0$, then $F = E - TS$ -->
$F = -TS$

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 $\sim \exp(-E\ /\ k_B T)$

----> $\mathcal{P}(x) \sim \exp(-k_{sp}x^2/2k_B T)$. (15)

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

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

Hence

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

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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, $<r_{ee}^2>$ = 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

$$x/L_c = (2\xi_p / 3k_B T)\, f. \tag{17}$$

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 Grün, 1942; James and Guth, 1943 (see also Flory, 1953, p. 427) have shown that a chain of rigid rods obeys

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

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

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

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):

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

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

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