Persistent or Wormlike Chains

In this appendix, we consider the stiffness of chains. Polyethylene is an example of a flexible chain. DNA is an example of a stiff chain. The basic tool we need is the $\langle r^2 \rangle$ equation derived in this chapter.

Flexible Chain	Stiff Chain
$\sqrt{\langle r^2 \rangle} \approx n^{1/2}$ or $n^{3/5}$ (theta or good) (1)	$\sqrt{\langle r^2 \rangle} \approx n$ (2)

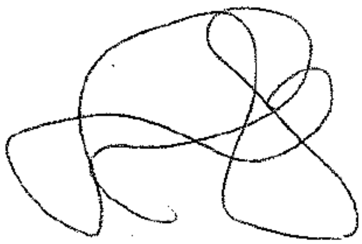
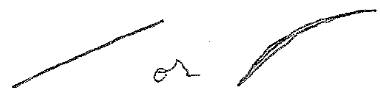

	

Fig 1	Fig 2

Intrinsic vs. Extrinsic: Flexibility vs Flex

A piece of steel tubing might seem to be rigid and inflexible, but imagine the same substance one mile long. It absolutely will bend! A short piece has the same ability to flex as the mile-long piece—flexibility is an *intrinsic* property—but it just has no opportunity to flex.

Flexibility: ability to flex (intrinsic property of a given material, like density)
Flex: actual, observable flexing (extrinsic property, depends on length)

You cannot easily see something "rigid" bend unless it is long enough. Many high-performance polymers fall into the "almost long enough to see" category.

Persistence Length, a: an intrinsic property that characterizes the ability to flex.

Definition: For a given material (polymer chain, railroad track, lightning bolt—you name it) persistence length *a* is the projection an infinitely long filament makes on an axis drawn tangent to one end of the filament.

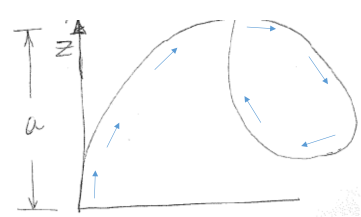
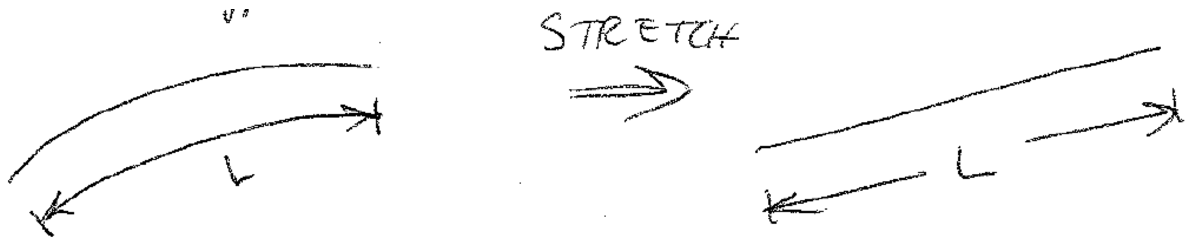


Figure 3. A chain makes a projection onto an axis drawn tangent to one of its ends.

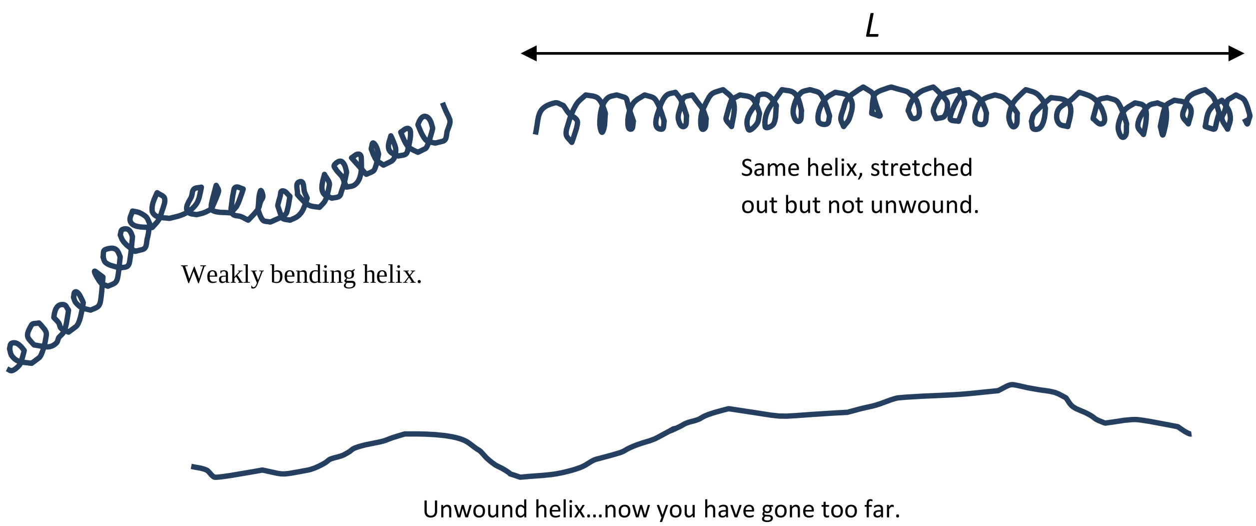
Imagine the filament in Figure 3 is just part of an infinitely long chain. You cannot see the individual chemical bonds…they are tiny on this scale. Might as well be a strand of rope or a piece of spaghetti. Each vector (little arrows) makes a projection onto the z axis, but after some length, these begin to cancel out! You can already see right-going arrows canceling out with left-pointing arrows. But the net projection is not zero because the chain is persistent at its end. The persistence length *a* is the net projection along the z-axis (which is drawn parallel to one end of the chain) of the whole infinitely long chain. It is drawn almost correctly.

Contour Length, L

Definition: the contour length is the maximum separation of chain ends that could be achieved without *seriously* disrupting the bond structure. These two chains below are the same length. The one on the right has slightly larger end-to-end distance. Measuring persistence length is all about being able to measure that small difference.



Many persistent chains are helical…like springs. DNA is like this, and synthetic polypeptides too. You are allowed to draw the helix into a straight line…but you are not allowed to unwind it!



The contour length is proportional to the molecular weight. The persistence length, by definition, should not be proportional to the molecular weight…it's an intrinsic property! If you measured (nevermind how) the persistence length and experimentally found it to depend on molecular weight, it would mean that the chain is somehow changing due to its length. This *can* happen; for example, high-*M* chains might show branching that is not present in smaller samples of the same polymer. A branched chain is a fundamentally different kind of object, and the persistent chain model should not be applied anymore.

Wormlike!

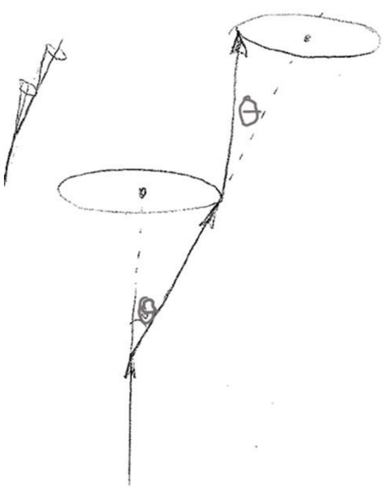
The persistent chain model is also called the wormlike chain model. Some people may say Kuhn model. I have always thought wormlike was kind of odd: worms easily bend. But normally, they do go straight for a fair distance. A Bing image search will confirm this: http://www.bing.com/images/search?q=worm&FORM=HDRSC2

Mathematical Model for Wormlike/Semiflexible Chains

The model we use is identical to the freely rotating chain model introduced in the main chapter. Indeed, that FR model is useless for describing typical vinyl chains (you need the correlations between bonds) but it is very valuable for these wormlike chains. There is no difference in the model, but instead of bond angle supplements like 70.6^o (i.e., 180^o-109.4^o, the tetrahedral angle) now our bond angle supplement θ is vanishingly small.

Wormlike Chain Model = Freely Rotating Chain Model in the limit of very small bond angle supplements, θ.

We could immediately write the equation from before:

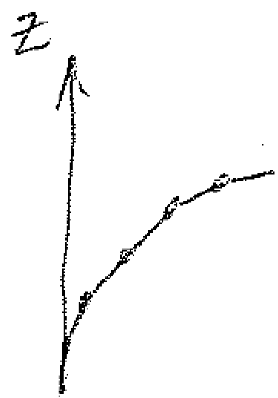


$$\langle r^2 \rangle = nl^2 \left(\frac{1+\gamma}{1-\gamma}\right) - \frac{2l^2(1-\gamma^n)}{(1-\gamma)^2} \quad (3)$$

where $\gamma = \cos\theta$

The only problem with this is that we don't know what n, γ and ℓ are. It does not matter, though. What we need is n equal segments of some arbitrary length l, with an arbitrary but small angle θ as their supplement. Neither ℓ nor θ bear any relation to an actual chemical bond. These three parameters, n, ℓ and θ, are about to be trimmed down to two parameters, a and L. Meanwhile, they just make the FR model work for us.

> Essentially, all models are wrong, but some are useful.
>
> --George E. P. Box, Statistician



Before we transform the above equation into one containing parameters *a* and *L*, it will be helpful to take a little detour by calculating the average projection, $\langle z_n \rangle$ of *n* (whatever that is) bonds (whatever they are) onto the *z* axis. Remember, *z* is drawn to be a tangent to one end of the chain.

Define: $\langle z_n \rangle$ = projection made by an *n*-bond molecule onto the *z*-axis.

The same logic used in the FR calculation applies: each bond makes a projection onto its predecessor equal to its length times the cosine of our angle θ. On average, these get re-projected by the preceding bond onto *that* bond's predecessor. Eventually, we get the projection onto the first bond:

$$\langle \cos\theta_{1i} \rangle = \cos^{i-1}\theta \qquad (4)$$

So…
$$\langle z_n \rangle = \sum_{i=1}^{n} l_i \langle \cos^{i-1}\theta \rangle \qquad (5)$$

If all the bonds are the same length, we can factor them out:

$$\Rightarrow\ l\sum_{i=1}^{n}\cos^{i-1}\theta \qquad (6)$$

We recognize this as almost a geometric series types of sum. Let's divide & multiply a cos(θ) term to make it easier.

$$\Rightarrow\ \frac{l}{\cos\theta}\sum_{i=1}^{n}(\cos\theta)^{i} \qquad (7)$$

We can evaluate this sum:

$$S_n = \sum_{i=1}^{n}\cos\theta = \cos\theta + (\cos\theta)^2 + \ldots + (\cos\theta)^n \qquad (8)$$

Multiply both sides by cos(θ):

$$(\cos\theta)S_n \rightarrow (\cos\theta)^2 + \ldots + (\cos\theta)^n + (\cos\theta)^{n+1} \qquad (8)$$

Solve: $$\sum_{i=1}^{n}\cos\theta = \frac{\cos\theta - (\cos\theta)^{n+1}}{1-\cos\theta} = \frac{\cos\theta}{1-\cos\theta}(1-(\cos\theta)^n) \qquad (9)$$

$$\langle z_n \rangle = \frac{l}{\cos\theta}\frac{\cos\theta}{1-\cos\theta}(1-\cos^n\theta) \qquad (10)$$

$$\langle z_n \rangle = \frac{l(1-\cos^n\theta)}{1-\cos\theta} \qquad (11)$$

Consideration of Eq. 12 in the infinite chain and finite chain extremes will permit identification of a persistence length relative to θ and relative to $<r^2>$, respectively. First the infinite limit: if $n \rightarrow \infty$ the second term of the numerator goes to zero.

By its definition, the persistence length $a = \lim_{n \to \infty} \langle z_n \rangle \Rightarrow \dfrac{l}{1-\cos\theta}$ (12)

Now the finite limit: By design of this development, θ is small.

We can use a Taylor's expansion to get rid of the cosine term.

$$\cos\theta = \cos(0) + \left(\frac{d}{d\theta}\cos\theta\right)\Big|_{\theta=0}\theta + \frac{1}{2!}\left(\frac{d^2}{d\theta^2}\cos\theta\right)\Big|_{\theta=0}\theta^2$$

Evaluating the series at $\theta = 0$:

$$\cos\theta \approx 1 - \frac{\theta^2}{2} \equiv e^{\frac{-\theta^2}{2}} \qquad (13)$$

Just rearrange:

$$1-\cos\theta \approx \frac{\theta^2}{2} \qquad (14)$$

But now look at Eq. 12:

$$1-\cos\theta = \frac{l}{a} \qquad (15)$$

We have two forms of $1 - \cos\theta$. Equating them:

$$\frac{l}{a} \approx \frac{\theta^2}{2} \qquad (16)$$

We can go back up to Eq. 11 and put in these relations to reach:

$$\langle z_n \rangle = \frac{l(1-\cos^n\theta)}{1-\cos\theta} \Rightarrow \frac{l\left(1-e^{\frac{-n\theta^2}{2}}\right)}{l/a} \qquad (17)$$

Now cancel the l terms, use Eq. 16 in the exponent, and recognize that, even though we don't know what n and $\boldsymbol{\ell}$ are, we do know their product is the contour length L.

$$\langle z_n \rangle = a(1-e^{\frac{-nl}{a}}) \overset{nl=L}{\Rightarrow} a\left(1-e^{\frac{-L}{a}}\right) \qquad (18)$$

Hey! The arbitrary stuff—θ, n and $\boldsymbol{\ell}$—is all gone! We have persistence length in terms of average projection and contour length. There is only one problem: Eq. 18 cannot be solve analytically. So, if you knew $\langle z_n \rangle$ and L—which is not so hard to do if you can physically see the chains—you must try different values of persistence length a until the left-hand and right-hand sides of Eq. 18 agree. You need a numerical solution.

Now we have to connect this to $\langle r^2 \rangle$. This is a 4-step process:

1. We will put $\boldsymbol{\ell}$ and θ back in for awhile (sad).
2. We will recall that FR formalism.
3. We will remove l and θ again
4. We'll see that we have connected a to things that are potentially measurable, L and $\langle r^2 \rangle$.

We had the general FR result already in Eq. 3 (and in the main part of the chapter). Here it is again (keep old equation number).

$$\langle r^2 \rangle = nl^2\left(\frac{1+\gamma}{1-\gamma}\right) - \frac{2l^2(1-\gamma^n)}{(1-\gamma)^2} \qquad (3)$$

where $\gamma = \cos\theta$

By design of this development:

$$\langle r^2 \rangle_{worm} = \lim_{\substack{\theta\to 0\\(\gamma\to 1)}} \langle r^2 \rangle_{\text{Freely Rotating}} \qquad (19)$$

From Eq. 15:

$$\frac{l}{a} = 1-\gamma \approx \frac{\theta^2}{2} \qquad (20)$$

Re-arranging:

$$\gamma = 1-\frac{l}{a} \qquad (21)$$

Put into Eq. 3 at some locations (denominators), expand the second term:

$$\langle r^2 \rangle_{worm} = nla(1+\gamma) - 2a^2\gamma + 2a^2\gamma^{n+1} \qquad (22)$$

$$\underset{\substack{\text{except in}\\ \text{last term}}}{\overset{use\,\gamma=1-l/a}{\Rightarrow}} nla\left(2-l/a\right)-2a^2\left(1-1/a\right)+2a^2\gamma^{n+1} \qquad (23)$$

$$\underset{\text{terms}}{\overset{\text{write out}}{\Rightarrow}} 2nla - nl^2 - 2a^2 + 2al + 2a^2\gamma^{n+1} \qquad (24)$$

Move terms around:

$$\Rightarrow\ 2nla - 2a^2 + \left(2al - nl^2\right) + 2a^2\gamma^{n+1} \qquad (25)$$

The term in parentheses is smaller than the others (**ℓ** is small, *n* ***ℓa*** is like *La*, which is large, etc.). We'll let it hang around for a while, but we can expect it might be "droppable" whenever ***a*** is substantial.

Now let us look at last term, $2a^2\gamma^{n+1}$

$$\Rightarrow 2a^2\gamma\gamma^n$$

$$\Rightarrow 2a^2\gamma\left(1-\frac{l}{a}\right)^n \qquad (26\text{ a-d})$$

$$\overset{\text{if } l/a<<1}{\Rightarrow}\ 2a^2\gamma\left(e^{-l/a}\right)^n$$

$$\Rightarrow 2a^2\gamma\, e^{-nl/a}$$

In the four lines above, we used relations above plus the Taylor expansion for an exponential, keeping only low terms because *a* >> l in most cases.

$$\left\langle r^2\right\rangle_{worm} \Rightarrow 2nla - 2a^2 + \left(2al - nl^2\right) + 2a^2\gamma\, \mathrm{e}^{-nl/a}$$

$$\overset{factor\,2a}{\Rightarrow}\ 2a\left[nl - a + a\gamma\, \mathrm{e}^{-nl/a}\right] + \left(2al - nl^2\right) \qquad (27\text{ a-b})$$

Using the simplification $l/a << 1$ implies $\gamma \approx 1$, so we might as well go with that in that gamma term just ahead of the exponential. It's only one power of gamma, so won't cause much trouble. Also, $nl = L$

$$\left\langle r^2\right\rangle_{worm} \approx 2a\left[L - a + a\, \mathrm{e}^{-L/a}\right] + \left[2al - nl^2\right] \qquad (28)$$

Let's just drop that last term in brackets for the reasons we already mentioned: too small compared to the lead term.

$$\langle r^2 \rangle = 2a\left[L - a + a\,\mathrm{e}^{-L/a}\right] \qquad (29)$$

We should do three checks.

First, let us expand this in the rodlike limit, $L << a$, to see if it behaves sensibly. To do this, expand the exponential, keeping a few terms.

$$\langle r^2 \rangle \Rightarrow 2a\left[L - a + a\left(1 - \frac{L}{a} + \frac{1}{2}\left(\frac{L}{a}\right)^2\right)\right]$$

$$\Rightarrow 2a\left[L - a + a - L + \frac{L^2}{2a}\right] \qquad (30)$$

$$\langle r^2 \rangle = L^2 \qquad \textit{as it should for a rod}$$

Second, let's go back to Eq. 28 and check that the term we dropped, $(2a\ell - n\ell^2)$, is really negligible under typical conditions.

Try a = 10 Å (relatively short, typical of vinyl polymers)
L=100 Å , l = 1.5 Å
Then $n \cong 100/1.5 = 67$
Then the first term: 1800
Second term: -120 …. Negligible!

Third, let's look at the coil-like limit, $a << L$. In that case, a and $a\mathrm{e}^{-L/a}$ are negligible.

$$\langle r^2 \rangle = 2aL = 2anl \equiv C_\infty nl^2$$

(30 a-b)

$$\textit{where } C_\infty = 2a/l$$

So, that's good: we have connected characteristic ratio C_∞ to persistence length when persistence length is small. That concludes our mathematical analysis of the wormlike chain molecule.

Kuhn Length

The last thing we must do is a bit of tradition. It's also fun and instructive. When a filament is very long or very flexible ($a << L$ as in Eq. 30), it bends and looks for all the world like a random flight polymer. It then becomes interesting to define the Kuhn segment length, l_k, and a number of these Kuhn lengths, N_k, and force-fit it into a freely jointed equation (N_k and ℓ_k are defined to fit the FJ style).

$$\langle r^2 \rangle = l_k{}^2 N_k \equiv 2anl = 2aL \qquad (31)$$

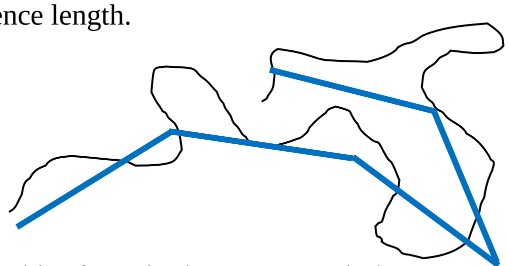
The constant thing here is the contour length. It is the product of the imaginary $n\ell$ or the imaginary $N_k\ell_k$ terms.

$$N_k l_k = L = nl$$

$$So \langle r^2 \rangle = Ll_k = 2aL$$

$$\Rightarrow l_k = 2a$$

The Kuhn length is twice the persistence length. As the sketch below shows, the Kuhn lengths can bend any old way, because it's a FJ model by design, but do not match the chain. They are twice as long as the persistence length.



Lastly, a bit of terminology…or symbology anyway. Sometimes instead of a Kuhn length, we have the Kuhn parameter, l, its inverse.

$$l_k = \lambda^{-1}$$
$$\to \lambda^{-1} \textit{ is a length}$$
$$2a\lambda = 1$$

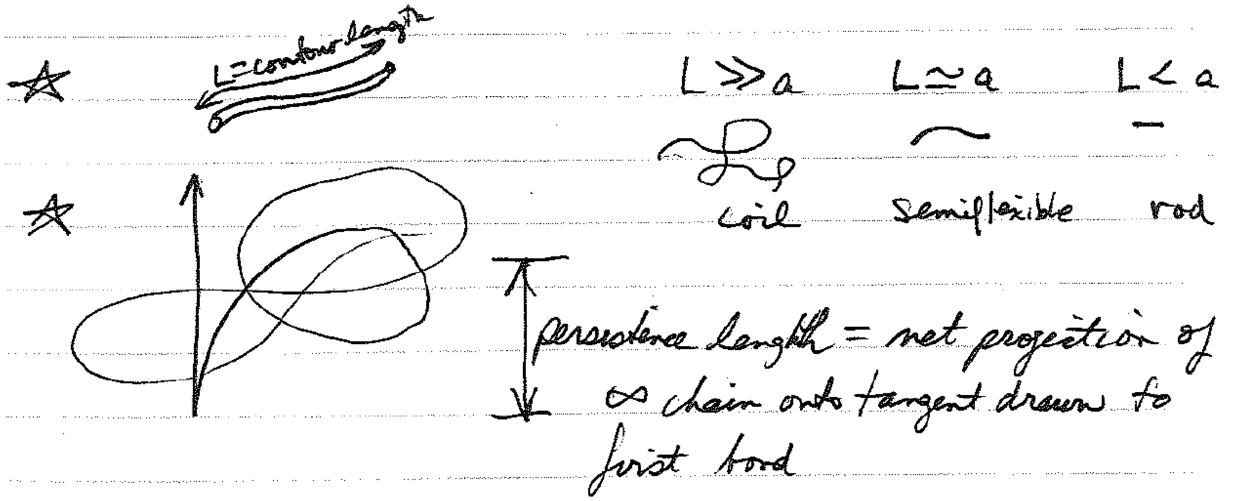
Radius of gyration

Normally, the thing light scattering can measure is Rg2. We won't develop this equation, but you can find it in Yamakawa's book (Eq. 9.108 p. 56)

$$\langle s^2 \rangle = R_g{}^2 = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2}\left(1 - e^{-2\lambda L}\right)$$

$$with\ 2a\lambda = 1 \text{ or } \lambda = \frac{1}{2a}$$

Summary



Acknowledgment

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