[pex29] Kuhn segment length of ideal polymer chain

Flexibility is an intrinsic property of polymers. Consider an ideal polymer chain with N links of length a. Its contour length is $L = Na$. If we divide that chain into segments of length $l \geq a$ then, with growing size of these segments, the joints become effectively less constrained and less stiff. At the Kuhn segment length l_K the joints become effectively free. The mean-square distance of a freely-jointed chain (FJC) is $\langle R^2 \rangle = Na^2 = La$ [pln50]. The natural definition of the Kuhn segment length, therefore, is [pln51]

$$l_\mathrm{K} \doteq \frac{\langle R^2 \rangle}{L}.$$

The Kuhn segment length l_K is a measure for the stiffness of the polymer chain just as the persistence length l_p investigated in [pex28] is. However, the two measures are not identical. The Kuhn segment length is easier to determine experimentally and theoretically but the persistence length has a more direct physical meaning. Here we explore the functional relation between l_K and l_p for an ideal polymer chain with persistent flexibility. On a mesoscopic scale we describe the conformation of the polymer by a vector function $\vec{r}(s)$ and replace the local bond vector $\vec{a}_i$ by the vector function $\vec{u}(s) = d\vec{r}/ds$ with s as defined in [pex28]. The end-to-end distance vector and its mean-square value can thus be expressed as follows:

$$\vec{R} = \int_0^L ds\, \vec{u}(s), \quad \langle R^2 \rangle = \int_0^L ds \int_0^L ds' \langle \vec{u}(s) \cdot \vec{u}(s') \rangle.$$

To calculate the latter we infer from [pex28] the relation

$$\langle \vec{u}(s) \cdot \vec{u}(s') \rangle = \langle \cos\theta(s - s') \rangle = e^{-|s-s'|/l_\mathrm{p}}.$$

Perform the double integral to obtain an analytic expression of the scaled Kuhn segment length l_K/L as a function of the scaled persistence length l_p/L. Show in particular that for very long polymers ($L \gg \tilde{l}$), we have $l_\mathrm{K} \simeq 2l_\mathrm{p}$ and for very short polymers ($L \ll l_\mathrm{p}$) we have $l_\mathrm{K} \simeq L$. Plot l_K/L versus l_p/L over the range $0 < l_\mathrm{p}/L < 3$ to illustrate this behavior.

[adapted from Grosberg and Khokhlov 1994]

Solution: