SIF40AH/DIF4997
Nano-particle and polymer physics I
EXERCISE 2

According to the lecture notes (Ch. 2.6.2 of version AM11sep02) the classical definiton of the persistence length, $L^{(\mathrm{p})}$, of a segmented linear polymer, $L^{(\mathrm{p})}$ equals the projection of the end-to-end vector $\vec{\boldsymbol{r}}_N - \vec{\boldsymbol{r}}_1 = \sum_{k=1}^{N-1} \vec{Q}_k$ on the unit vector of connector number one in the limit of an infinitely long chain

$$L^{(\mathrm{p})} := \lim_{N\to\infty} \left\langle |Q_1|^{-1} \vec{\boldsymbol{Q}}_1 \cdot \sum_{k=1}^{N-1} \vec{\boldsymbol{Q}}_k \right\rangle = \lim_{N\to\infty} |Q_1|^{-1} \sum_{k=1}^{N-1} \left\langle \vec{\boldsymbol{Q}}_1 \cdot \vec{\boldsymbol{Q}}_k \right\rangle . \tag{1}$$

where $\langle \ldots \rangle$ = time average = assembly average for ergodic systems.

The *Flory definition of persistence length* instead refers to the projection onto segment i where $1 \ll i \ll N$. This definition avoids end-effects when $N \to \infty$. When $|\vec{\boldsymbol{Q}}_k| = Q$ and $\vec{\boldsymbol{Q}}_1$ lies along the local x-axis Eq. (1) yields

$$L^{(\mathrm{p})} = Q \lim_{N\to\infty} \sum_{k=1}^{N-1} [1,0,0] \left\langle \prod_{m=1}^{k-1} \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m \right\rangle \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \tag{2}$$

where the product of the last two factor equals $\vec{\boldsymbol{Q}}_k$ in the local coordinate system of vector $\vec{\boldsymbol{Q}}_1$. $\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m$ is the transformation matrix from coordinate system $m+1$ to m:

$$\vec{Q}_k = \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_1 \cdot \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_2 \cdots \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_{k-1} \cdot Q \cdot \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = Q \prod_{m=1}^{k-1} \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m \cdot \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \tag{3}$$

Further, if there are the intramolecular interactions only between nearest neighbour segments, the averages factorize so that the above expression can be rewritten as

$$L^{(\mathrm{p})} = Q \lim_{N\to\infty} \sum_{k=1}^{N-1} [1,0,0] \prod_{m=1}^{k-1} \left\langle \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m \right\rangle \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}. \tag{4}$$

A) Prove the relation

$$\left\langle \prod_{m=1}^{k-1} \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m \right\rangle = \prod_{m=1}^{k-1} \left\langle \overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m \right\rangle \tag{5}$$

used to deduce Eq. (4) from Eq. (2). Detail all assumptions required.

B) Use the result above to show that the expression for the persistence length of the freely rotating Kirkwood-Riseman chain equals

$$L^{(\mathrm{p})} = \frac{Q}{1-\cos\xi}$$