FY8201 / TFY8 **Nanoparticle and polymer physics I**
SOLUTION of EXERCISE 2

Eq. (x.x) refers to version AM24nov05 of lecture notes: "Nanoparticle and polymer physics".

First we repeat given equations:

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

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

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

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

We assume low concentrations of polymers so that only intramolecular (and no intermolecular) forces determine the molecular configuration $\vec{Q}_k$. Further we assume that there are interaction only between the nearest neighbour segments in the polymer chain . Thermal average is then expressed by

$$\langle B\rangle = \frac{\int\cdots\int B\exp\{-\mathcal{H}(\vec{P},\vec{Q})\beta\}\,\mathrm{d}\vec{P}\mathrm{d}\vec{Q}}{\int\cdots\int\exp\{-\mathcal{H}(\vec{P},\vec{Q})\beta\}\,\mathrm{d}\vec{P}\mathrm{d}\vec{Q}} \tag{5}$$

where $\beta = (k_\mathrm{B}T)^{-1}$ and the Hamiltonian $\mathcal{H}$ is a function of nearest neighbour vectors

$$\mathcal{H} = \sum_{i=1}^{N-2}h_i(\vec{Q}_i,\vec{Q}_{i+1}) = \sum_{i=1}^{N-2}h_i(\vec{Q}_i,\,\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_i\cdot\vec{Q}_{i+1}) \tag{6}$$

where h_i are any functions (not required to be specified). Note the notation: In the first sum $\vec{Q}_i$ and $\vec{Q}_{i+1}$ are given relative to their respective local coordinate systems, while in the last sum they are given respective to the *same* coordinate system, namely the coordinate system of segment vector number i.

The thermal averaging in Eq. (2) now yields

$$\left\langle\prod_{m=1}^{k-1}\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m\right\rangle = \frac{1}{Z}\int\int\prod_{m=1}^{k-1}\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m\exp\{-\mathcal{H}\beta\}\,\mathrm{d}\vec{P}\mathrm{d}\vec{Q} \tag{7}$$

where Z is the normalization constant (the partition function). Insertion of $\mathcal{H}$ from Eq. (6) yields

$$\begin{aligned}\left\langle\prod_{m=1}^{k-1}\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m\right\rangle &= \frac{1}{Z}\int\int\left(\prod_{m=1}^{k-1}\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m\right)\exp\{-\beta\sum_{i=1}^{N-2}h_i(\vec{Q}_i,\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_i\ \vec{Q}_{i+1}\}\,\mathrm{d}\vec{P}\mathrm{d}\vec{Q}\\ &= \frac{1}{Z'}\int\int\prod_{m=1}^{k-1}\left(\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m\exp\{-\beta\cdot h_m(\vec{Q}_m,\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_m\ \vec{Q}_{m+1}\}\right)\,\mathrm{d}\vec{P}\mathrm{d}\vec{Q}\end{aligned} \tag{8}$$

where all integrals containing h_i with $i\in[k,N-2]$ have been cancelled by the corresponding integrals in Z. Noting that only h_1 contains $\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_1$, h_2 contains $\overset{\Rightarrow(\xi)}{\boldsymbol{\Omega}}_2$ etc., we obtain:

$$\left\langle \prod_{m=1}^{k-1} \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \right\rangle = \frac{1}{Z'} \prod_{m=1}^{k-1} \left(\int\int \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \exp\{-\beta \cdot h_m(\vec{Q}_m, \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \vec{Q}_{m+1}\} \, \mathrm{d}\vec{P}\mathrm{d}\vec{Q} \right) \tag{9}$$

$$= \underline{\prod_{m=1}^{k-1} \left\langle \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \right\rangle}. \tag{10}$$

B) In the Kirkwood-Riseman chain $\vec{Q}_{k+1}$ can be rotated freely an angle ξ_{k2} around $\vec{Q}_k$ with a fixed angle $\xi_{k1} = \xi$. As the angle ξ_{k2} is free to rotate between 0 and 2π, the Hamiltonian $\mathcal{H}$ does not depend on ξ_{k2} and the average is zero:

$$\langle \cos\xi_{k2} \rangle = \frac{1}{Z} \int \cdots \int \cos\xi_{k2} \exp\{-\mathcal{H}(\vec{P}, \vec{Q})\beta\} \mathrm{d}\xi_{k2} \, \mathrm{d}\vec{P}\mathrm{d}\vec{Q} = 0 \tag{11}$$

$$\tag{12}$$

And similarly $\langle \sin\xi_{k2} \rangle = 0$. Therefore (from Eq. (2.53))

$$\left\langle \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \right\rangle = \begin{bmatrix} \cos\xi & -\sin\xi & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \equiv \overset{\Rightarrow}{\mathbf{\Omega}} \tag{13}$$

From the result in A) of this exercise we get

$$\left\langle \prod_{m=n}^{p} \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \right\rangle = \prod_{m=n}^{p} \left\langle \overset{\Rightarrow(\xi)}{\mathbf{\Omega}}_m \right\rangle = \prod_{m=n}^{p} \overset{\Rightarrow}{\mathbf{\Omega}} = \overset{\Rightarrow(p-n+1)}{\mathbf{\Omega}} \tag{14}$$

Inserted in Eq. (4) for persistence length:

$$L^{(\mathrm{p})} = Q \lim_{N\to\infty} \sum_{k=1}^{N-1} [1, 0, 0] \, \overset{\Rightarrow(k-1)}{\mathbf{\Omega}} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = Q \lim_{N\to\infty} \sum_{k=1}^{N-1} (\cos\xi)^{k-1}$$

$$= Q \sum_{k=1}^{\infty} (\cos\xi)^{k-1} = Q(1 + \cos\xi + \cos^2\xi + \cdots) = \underline{\frac{Q}{1 - \cos\xi}}. \tag{15}$$

The sum converges for $|\cos\xi| < 1$.

An alternative calculation according to Doi and Edwards

The average of the projection of $\vec{Q}_k$ on $\vec{Q}_{k-1}$ equals $\langle \vec{Q}_k \cdot \vec{Q}_{k-1} \rangle = Q^2 \cos\xi$, provided all Q_m where $m \neq k$ are being kept constant. Repeating this projection $k-1$ times we obtain $\langle \vec{Q}_k \cdot \vec{Q}_1 \rangle = Q^2 (\cos\xi)^{k-1}$.

From the definition in Eq. (1) we get

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

$$= Q \sum_{k=1}^{\infty} (\cos\xi)^{k-1} = \frac{Q}{1 - \cos\xi}, \tag{16}$$

as above.