FY8201 / TFY8 **Nanoparticle and polymer physics I**
SOLUTION of EXERCISE 3

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

A) The segment length $Q = 10$ nm. Note: $N_s = 100$ segments means $N = N_s + 1 = 101$.

i) **Contour length:** $\underline{L^{(c)}} = (N-1)Q = 100 \times 10 \text{ nm} = 1000 \text{ nm} = \underline{1,0\ \mu\text{m}}$

ii) **Average end-to-end vector:**

$$\langle \vec{\boldsymbol{R}}_{1N} \rangle = \int \vec{\boldsymbol{R}}_{1N}\ p^{(\text{eq})}(\vec{\boldsymbol{R}}_{1N})\ \mathrm{d}\vec{\boldsymbol{R}}_{1N}$$

where (Eq. (2.93))

$$p^{(\text{eq})}(\vec{\boldsymbol{R}}_{1N})\mathrm{d}\vec{\boldsymbol{R}}_{1N} = \left(\frac{3}{2\pi(N-1)Q^2}\right)^{3/2} \exp\left\{-\frac{3R_{1N}^2}{2(N-1)Q^2}\right\} \cdot \mathrm{d}x\mathrm{d}y\mathrm{d}z$$

Because of the symmetry of $p^{(\text{eq})}$ integration from $-\infty$ to ∞ yields

$$\underline{\langle \vec{\boldsymbol{R}}_{1N} \rangle \ = \ 0}$$

iii) **Average end-to-end distance:**

$$\langle R_{1N} \rangle = \int_0^\infty R_{1N}\, p^{(\text{eq})}(R_{1N})\ \mathrm{d}R_{1N}$$

where (e.g. from "Molekylær biofysikk" Eq. (7.29) or "Bionanoparticle physics", Eq. (6.3-29))

$$p^{(\text{eq})}(R_{1N})\mathrm{d}R_{1N} = 4\pi R_{1N}^2 \left(\frac{3}{2\pi(N-1)Q^2}\right)^{3/2} \exp\left\{-\frac{3R_{1N}^2}{2(N-1)Q^2}\right\} \cdot \mathrm{d}R_{1N}\,.$$

From tables:

$$\int_0^\infty r^3 \exp\{-\lambda r^2\} = \lambda^{-2}/2$$

which yields

$$\underline{\langle R_{1N} \rangle} = \sqrt{\frac{8}{3\pi}} \cdot \sqrt{N-1} \cdot Q = \underline{92 \text{ nm}}$$

iv) **Average quadratic end-to-end distance**.

$$\begin{aligned}\langle R_{1N}^2 \rangle &= \int R_{1N}^2\ p^{(\text{eq})}(\vec{\boldsymbol{R}}_{1N})\ \mathrm{d}\vec{\boldsymbol{R}}_{1N} \\ &= \int R_{1N}^2 \left(\frac{3}{2\pi(N-1)Q^2}\right)^{3/2} \exp\left\{-\frac{3R_{1N}^2}{2(N-1)Q^2}\right\} \mathrm{d}\vec{\boldsymbol{R}}_{1N}\end{aligned}$$

With $\mathrm{d}\vec{\boldsymbol{R}}_{1N} = 4\pi R_{1N}^2 \mathrm{d}R_{1N}$ (spherical symmetry) and integration from $R_{1N} = 0$ to ∞ we obtain, using tables:

$$\langle R_{1N}^2 \rangle = (N-1)\ Q^2 = 100 \times 10^2\ \text{nm}^2 = 10000\ \text{nm}^2 \quad \Rightarrow \quad \underline{\sqrt{\langle R_{1N}^2 \rangle} = 100\ \text{nm}}$$

$\langle R_{1N}^2 \rangle$ can also be calculated alternatively:

$$\langle R_{1N}^2 \rangle = \Sigma_i^{100}\Sigma_j^{100}\langle \vec{\boldsymbol{Q}}_i \cdot \vec{\boldsymbol{Q}}_j \rangle = \Sigma_i^{100}\Sigma_j^{100}\delta_{ij} \cdot Q^2 = 100 \cdot Q^2$$

v) **Maximal stretch ratio:**

$$\frac{L^{(c)}}{\sqrt{\langle R_{1N}^2\rangle}} = \frac{1000\ \text{nm}}{100\ \text{nm}} = \underline{10}$$

vi) **Radius of gyration** (Eq. (2.152):

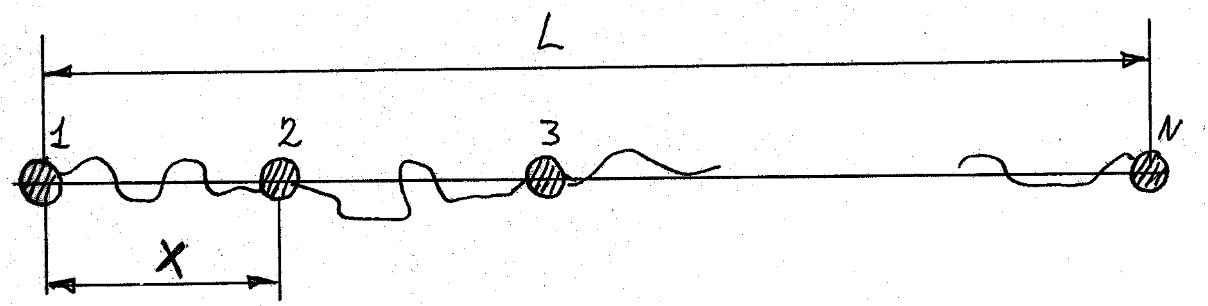
$$\left\langle R^{(G)2}\right\rangle_{\text{eq}} = \frac{N^2-1}{6N}Q^2 = \frac{1}{6}\frac{N+1}{N}\left\langle R_{1N}^2\right\rangle_{\text{eq}} = \frac{1}{6}\cdot\frac{102}{101}\cdot 10000\ \text{nm}^2 = 1683\ \text{nm}^2$$

$$\Rightarrow \underline{\sqrt{\langle R^{(G)2}\rangle_{\text{eq}}} = 41\ \text{nm}}$$

vi) **Spring stiffness (spring constant) when changing the end-to-end distance of the molecule:**

$$\begin{aligned} |k_s| &= \frac{F}{R_{1N}} = \frac{3k_BT}{(N-1)Q^2} \\ &= \frac{3\times 1.38\times 10^{-23}\ \text{Nm/deg}\times 300\ \text{deg}}{100\times 100\ \text{nm}^2} = \underline{1.2\times 10^{-6}\ \text{N/m}} \end{aligned} \tag{1}$$

B)



i) The Helmholtz free energy of each spring:

$$A = U_1 - T\cdot S = k_S/2\cdot(l - l_{\text{max}}/2)^2 - 0$$

This yields the average force between end points of the polymer

$$F = -\frac{\mathrm{d}A}{\mathrm{d}l} = -k_S\cdot(l - l_{\text{max}}/2) \quad \text{ie. } \underline{\text{spring constant}} = -\frac{\mathrm{d}F}{\mathrm{d}l} = \underline{k_S}$$

ii) When the potential equals U_2 the entropy of the spring determines the spring stiffness. The entropy $S(L)$ as function of the end-to-end distance L is calculated through $A(L) = U_1 - T\cdot S(L) = 0 - T\cdot S(L)$

The function $p^{(\text{eq})}(L)$ is the probability to find the end-to-end distance of the chain, L, within a certain length:

$$p^{(\text{eq})}(L) = \frac{\int\cdots\int_0^{l_{\text{max}}}\delta(L-\sum_{j=1}^{N_s}x_j)\mathrm{d}^{N_s}x}{\int\cdots\int_0^{l_{\text{max}}}\mathrm{d}^{N_s}x}$$

where $\delta(y)$ is Diracs delta function and N_s = no. of segments = 100. The delta function is on integral form expressed

$$\delta(y) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp\{iys\}\mathrm{d}s$$

Inserted in expression for $p^{(\mathrm{eq})}$ this yields

$$\begin{aligned} p^{(\mathrm{eq})}(L) &= \frac{1}{l_{\max}^{N_s}}\int\cdots\int_0^{l_{\max}} \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp\left\{i(L-\sum_j^{N_s} x_j)\cdot s\right\} \mathrm{d}s\,\mathrm{d}^{N_s}x \\ &= \frac{1}{2\pi\, l_{\max}^{N_s}}\int_{-\infty}^{+\infty} \exp\{iLs\}\left[\int_0^{l_{\max}} \exp\{-ix\cdot s\}\mathrm{d}x\right]^{N_s} \mathrm{d}s \end{aligned}$$

where we have assumed that the distribution of all segments are equal. We have also used the relation

$$\exp\{-i\sum_{j=1}^{N_s} x_j s\} = \prod_{j=1}^{N_s}\exp\{-ix_j s\} = [\exp\{-ixs\}]^{N_s}$$

Further calculations yield

$$\begin{aligned} \int_0^{l_{\max}} \exp\{-ixs\}\mathrm{d}x &= \frac{1}{is}\left[1-\exp\{-il_{\max}s\}\right] \\ &= \frac{1}{is}\exp\{-i\frac{l_{\max}}{2}s\}\left[\exp\{i\frac{l_{\max}}{2}s\}-\exp\{-i\frac{l_{\max}}{2}s\}\right] \\ &= \frac{2}{s}\exp\{-i\frac{l_{\max}}{2}s\}\sin\frac{l_{\max}}{2}s \\ &= l_{\max}\exp\{-i\frac{l_{\max}}{2}s\}\frac{\sin\frac{l_{\max}}{2}s}{\frac{l_{\max}}{2}s} \end{aligned}$$

Inserted in expression of $p^{(\mathrm{eq})}$ this yields

$$p^{(\mathrm{eq})}(L) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp\left\{i(L-N_s\frac{l_{\max}}{2})s\right\}\left(\frac{\sin\frac{l_{\max}}{2}s}{\frac{l_{\max}}{2}s}\right)^{N_s} \mathrm{d}s$$

$$\begin{aligned} \left(\frac{\sin xs}{xs}\right)^{N_s} &= \exp\left\{N_s\cdot\ln\left[\frac{\sin xs}{xs}\right]\right\} && \left(\text{series expansion of } \frac{\sin xs}{xs}\right) \\ &\simeq \exp\left\{N_s\cdot\ln\left[1-\frac{1}{3!}(xs)^2+\cdots\right]\right\} && (\text{series expansion of } \ln[1+x]) \\ &\simeq \exp\left\{N_s\cdot\left(-\frac{1}{3!}(xs)^2+\cdots\right)\right\} && \left(xs = \frac{l_{\max}}{2}\cdot s,\ \text{ assuming } xs \ll 1\right) \\ &\simeq \exp\{-\frac{N_s}{6}(\frac{l_{\max}}{2}s)^2\} \end{aligned}$$

Inserted in the expression of $p^{(\mathrm{eq})}$ this yields

$$p^{(\mathrm{eq})} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp\left\{i\left[L-N_s\frac{l_{\max}}{2}\right]s-\frac{N_s}{6}(\frac{l_{\max}}{2}s)^2\right\} \mathrm{d}s$$

From mathematical tables we find that for $a > 0$

$$\int_{-\infty}^{+\infty} \exp\{-(ax^2+2bx+c)\}\mathrm{d}x = \sqrt{\frac{\pi}{a}}\exp\left\{\frac{b^2-ac}{a}\right\}$$

Employed on the equation of $p^{(\mathrm{eq})}(L)$ and utilizing that $N_s \cdot l_{\max} = L_{\max}$, we get

$$\begin{aligned} a &= \frac{N_s}{6}\left(\frac{l_{\max}}{2}\right)^2 = \frac{1}{6N_s}(L_{\max}/2)^2 \\ 2b &= -i[L-N_s\, l_{\max}/2] = -i[L-L_{\max}/2] \\ c &= 0 \end{aligned}$$

$$\Rightarrow\quad p^{(\mathrm{eq})}(L) = \left(\frac{\pi}{\frac{1}{6N_s}(L_{\max}/2)^2}\right)^{1/2}\exp\left\{-\frac{\frac{1}{4}\cdot(L-L_{\max}/2)^2}{\frac{1}{6N_s}(L_{\max}/2)^2}\right\}$$

The average force between the endpoints of the chain is

$$\begin{aligned}
F(L) &= -\frac{\mathrm{d}}{\mathrm{d}L}A(L) = \frac{\mathrm{d}}{\mathrm{d}L}TS(L) \\
&= \frac{\mathrm{d}}{\mathrm{d}L}k_B T \ln Z = \frac{\mathrm{d}}{\mathrm{d}L}k_B T \ln\left[\mathrm{const}\cdot p^{(\mathrm{eq})}(L)\right] \\
&= k_B T \frac{\mathrm{d}}{\mathrm{d}L}\left[\mathrm{const} + \frac{1}{2}\cdot\mathrm{const} - \frac{\frac{1}{4}\cdot(L-L_{\mathrm{max}}/2)^2}{\frac{1}{6N_s}(L_{\mathrm{max}}/2)^2}\right] \\
&= -k_B T\cdot\frac{\frac{1}{2}\cdot(L-L_{\mathrm{max}}/2)}{\frac{1}{6N_s}(L_{\mathrm{max}}/2)^2},
\end{aligned}$$

finally yielding the spring stiffness

$$\underline{k_S} = -\frac{\mathrm{d}\,F(L)}{\mathrm{d}L} = \frac{k_B T}{\frac{1}{3N_s}(L_{\mathrm{max}}/2)^2} = \underline{\frac{3k_B T}{N_s(l_{\mathrm{max}}/2)^2}}. \tag{2}$$

This is a very interesting result as it proves that though the spring constant of each individual spring approaches zero (as $U_2 = 0$ for $l \in [0, l_{\mathrm{max}}]$), the spring constant of the complete chain does not vanish. This on condition that the individual springs has a maximal length, which in practice always is fulfilled. Such a molecule therefore is a pure entropy spring. For real polymers the spring potential is usually a mixture of a maximal stretching length, L_{max}, and a potential U_1 within this length.

Also note that by assuming a segment length $Q = l_{\mathrm{max}}/2$ for each spring, the spring stiffness in (2) equals the spring stiffness calculated for the chain molecule in Eq. (1) ($N_s = N - 1$). This is so because Eq. (1) is calculated assuming that the polymer is an entropy spring.