Chapter 28 - **FORM FACTORS FOR POLYMER SYSTEMS**

1. THE DEBYE FUNCTION FOR GAUSSIAN CHAINS

Polymer coils in theta solvents or in the melt state follow Gaussian chain statistics whereby the inter-monomer distance r_{ij} is given by the following Gaussian distribution function:

$$P(r_{ij}) = \left(\frac{3}{2\pi < r_{ij}^2 >}\right)^{3/2} \exp\left[-\frac{3r_{ij}^2}{2 < r_{ij}^2 >}\right]. \qquad (1)$$

Here $<r_{ij}^2>$ is the variance given in terms of the statistical segment length a as:

$$< r_{ij}^2 >= a^2 \,|\, i-j \,|. \qquad (2)$$

The single-chain form factor is given by:

$$P(Q) = \frac{1}{n^2}\sum_{i,j}^{n} < \exp[-i\vec{Q}.\vec{r}_{ij}] > \qquad (3)$$

$$= \frac{1}{n^2}\sum_{i,j}^{n} \int d\vec{r}_{ij} P(r_{ij}) \exp\left[-i\vec{Q}.\vec{r}_{ij}\right]$$

$$= \frac{1}{n^2}\sum_{i,j}^{n} \exp\left[-\frac{Q^2 < r_{ij}^2 >}{6}\right]$$

$$= \frac{1}{n^2}\sum_{i,j}^{n} \exp\left[-\frac{Q^2 a^2 \,|\, i-j \,|}{6}\right].$$

The following property of the Gaussian distribution has been used:

$$< \exp[-iQ_x x_{ij}] >= \exp\left[-\frac{Q_x^2 < x_{ij}^2 >}{2}\right] = \exp\left[-\frac{Q_x^2 < r_{ij}^2 >}{6}\right] \qquad (4)$$

$$< \exp[-i\vec{Q}.\vec{r}_{ij}] >= \exp\left[-\frac{Q^2 < r_{ij}^2 >}{6}\right].$$

The following general identity is used:

$$\sum_{i,j}^{n} F(|i-j|) = n + 2\sum_{k=1}^{n}(n-k)F(k). \qquad (5)$$

Assuming that the number of chain segments n is large (n>>1), one obtains the Debye function (Debye, 1947):

$$P(Q) = \frac{1}{n^2}\left\{n + 2\sum_{k=1}^{n}(n-k)\exp\left[-\frac{Q^2a^2k}{6}\right]\right\} \qquad (6)$$

$$P(Q) = \frac{2}{Q^4R_g^{\ 4}}\left[\exp(-Q^2R_g^{\ 2}) - 1 + Q^2R_g^{\ 2}\right].$$

The radius of gyration is given by $R_g = \sqrt{a^2n/6}$.

Small-Q and high-Q expansions of the Debye function are:

$$P(QR_g << 1) = 1 - \frac{Q^2R_g^{\ 2}}{3} \qquad (7)$$

$$P(QR_g >> 1) = \frac{2}{Q^2R_g^{\ 2}}.$$

Two approximations are included here for the Debye function:

$$P(Q) = \frac{1}{\left(1 + \frac{Q^2R_g^{\ 2}}{3}\right)} \qquad (8)$$

$$P(Q) = \frac{1}{\left(1 + \frac{Q^2R_g^{\ 2}}{2}\right)}.$$

The first form agrees better at low-Q and the second form agrees better at high Q.

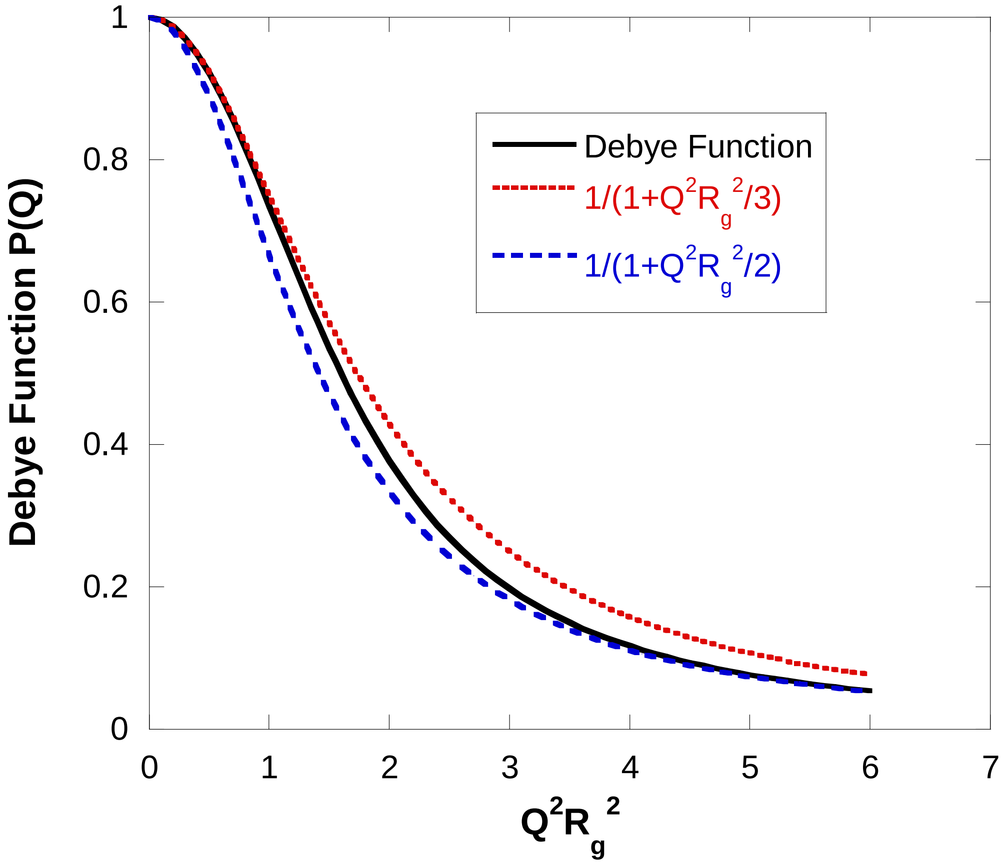


Figure 5: Variation of the Debye function P(Q) along with two approximations that bracket its variation. The form $1/\left(1+Q^2R_g^{\ 2}/3\right)$ is a good approximation at low-Q and the form $1/\left(1+Q^2R_g^{\ 2}/2\right)$ is a good approximation at high-Q.

Polymer chains are not characterized by uniform density. The form factor (Debye function) is not a square and cannot therefore be expressed as a square of the amplitudes.

2. SINGLE-CHAIN FORM FACTOR FOR GAUSSIAN CHAINS

Consider a flexible polymer coil where each monomer pair located a distance $\vec{r}_{ij}$ apart obeys the Gaussian distribution:

$$P(\vec{r}_{ij}) = \left(\frac{3}{2\pi < r_{ij}^{\ 2} >}\right)^{3/2} \exp\left[-\frac{3r_{ij}^{\ 2}}{2 < r_{ij}^{\ 2} >}\right]. \qquad (9)$$

The average of the segment inter-distances squares is kept in the general form:

$$< r_{ij}^2 >= a^2 |i-j|^{2\nu} . \tag{10}$$

ν is the excluded volume parameter. Note that $\vec{S}_{ij} = \vec{r}_{ij}$ in the notation used where $\vec{r}_{ij}$ is in the laboratory reference frame and $\vec{S}_{ij}$ is in the center-of-mass reference frame. Within this approach, the single-chain form factor is expressed as:

$$\begin{aligned} P(Q) &= \frac{1}{n^2}\sum_{i,j}^{n} < \exp[-i\vec{Q}.\vec{r}_{ij}] > \\ &= \frac{1}{n^2}\sum_{i,j}^{n}\int d\vec{r}_{ij}P(r_{ij})\exp\left[-i\vec{Q}.\vec{r}_{ij}\right] \\ &= \frac{1}{n^2}\sum_{i,j}^{n}\exp\left[-\frac{Q^2a^2}{6}|i-j|^{2\nu}\right]. \end{aligned} \tag{11}$$

Note that the monomer pair is always correlated through chain connectivity so that the simplifying approximation $P(Q) =| F(Q)|^2$ (which is made for uniform density objects) is not valid for polymers. The typical manipulations (as in the case of the Debye function described previously) are performed.

Assuming that the number of chain segments n is large (n >> 1), one obtains:

$$P(Q) = \frac{1}{n^2}2\sum_{k=1}^{n}(n-k)\exp\left[-\frac{Q^2a^2}{6}k^{2\nu}\right]. \tag{12}$$

Going to the continuous limit:

$$P(Q) = 2\int_0^1 dx\,(1-x)\exp\left[-\frac{Q^2a^2}{6}n^{2\nu}x^{2\nu}\right]. \tag{13}$$

This integral is “almost” analytical and can be expressed in terms of the incomplete gamma function:

$$\gamma(d,U) = \int_0^U dt\exp(-t)t^{d-1}. \tag{14}$$

The result is:

$$P(Q) = \frac{1}{\nu U^{1/2\nu}}\gamma(\frac{1}{2\nu},U) - \frac{1}{\nu U^{1/\nu}}\gamma(\frac{1}{\nu},U). \tag{15}$$

The modified variable is $U = \frac{Q^2 a^2 n^{2\nu}}{6}$.

The high-Q limit of this form is given by:

$$P(Q \to \infty) = \frac{1}{\nu U^{1/2\nu}} \Gamma(\frac{1}{2\nu}) - \frac{1}{\nu U^{1/\nu}} \Gamma(\frac{1}{\nu}). \qquad (16)$$

Here $\Gamma(x) = \gamma(x,\infty)$ is the gamma function. The asymptotic limit is dominated by the first term $\frac{1}{\nu U^{1/2\nu}} \Gamma(\frac{1}{2\nu})$ which varies like $U^{-1/2\nu} \sim Q^{-1/\nu}$.

Polymer chains follow Gaussian statistics in polymer solutions: they are swollen in good solvents, are thermally relaxed in “theta” solvents and partially precipitate in poor solvents. The familiar Debye function is recovered when $\nu = ½$.

3. OTHER POLYMER CHAIN ARCHITECTURES

Many polymer chain architectures exist: "stars" consist of many equal size branches connected to a central core, "combs" consist of side branches grafted onto a main chain, "rings" consist of looped chains, "gels" consist of highly branched structures that are grown outwardly (dendrimers are the most regular gels), "networks" consist of crosslinked systems that contain a large number of inter-connected structures, etc. These various polymer systems are made in the homopolymer form (all monomers are chemically identical) or copolymer form (each chain portion consists of blocks of monomers that are chemically different). Single-chain form factors for such architectures have been worked out and are summarized elsewhere (Burchard, 1983; Hammouda, 1993; Higgins-Benoit, 1994). Basic elements are included here.

In the same spirit used to derive the form factor for an isolated polymer chain (Debye function):

$$P(Q) = \frac{2}{Q^4 R_g^{\ 4}} \left[\exp(-Q^2 R_g^{\ 2}) - 1 + Q^2 R_g^{\ 2}\right], \qquad (17)$$

one can also derive the form factor amplitude for a polymer chain anchored at one end. In this case:

$$F(Q) = \frac{1}{n} \sum_{i}^{n} \exp\left[-\frac{Q^2 a^2 \,|\, i-1 \,|}{6}\right] \qquad (18)$$

$$= \frac{1-\exp\left[-Q^2 R_g{}^2\right]}{Q^2 R_g{}^2}.$$

Similarly, a propagation factor can be defined (involving no summation):

$$E(Q) = \exp[-Q^2 R_g{}^2]. \qquad (19)$$

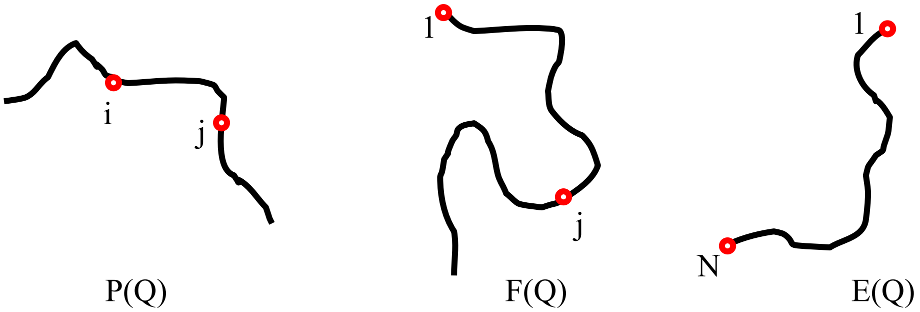


Figure 6: Schematic representation of the summation variables for the various scattering factors for Gaussian polymer chains.

The three scattering factors E(Q), F(Q), and P(Q) can be used to work out the form factors for many polymer architectures.

Consider the simple case of a diblock copolymer A-B consisting of two blocks with N_A-N_B segments. The various partial form factors follow:

$$P(Q) = n_A{}^2 P_{AA}(Q) + n_B{}^2 P_{BB}(Q) + 2n_A n_B P_{AB}(Q) \qquad (20)$$

$$P_{AB}(Q) = F_A(Q) F_B(Q).$$

Consider now an A-B-C triblock copolymer with n_A-n_B-n_C segments. The form factor involves many terms:

$$\begin{aligned} P(Q) &= n_A{}^2 P_{AA}(Q) + n_B{}^2 P_{BB}(Q) + n_C{}^2 P_{CC}(Q) \\ &+ 2n_A n_B P_{AB}(Q) + 2n_B n_C P_{BC}(Q) + 2n_A n_C P_{AC}(Q) \end{aligned} \qquad (21)$$

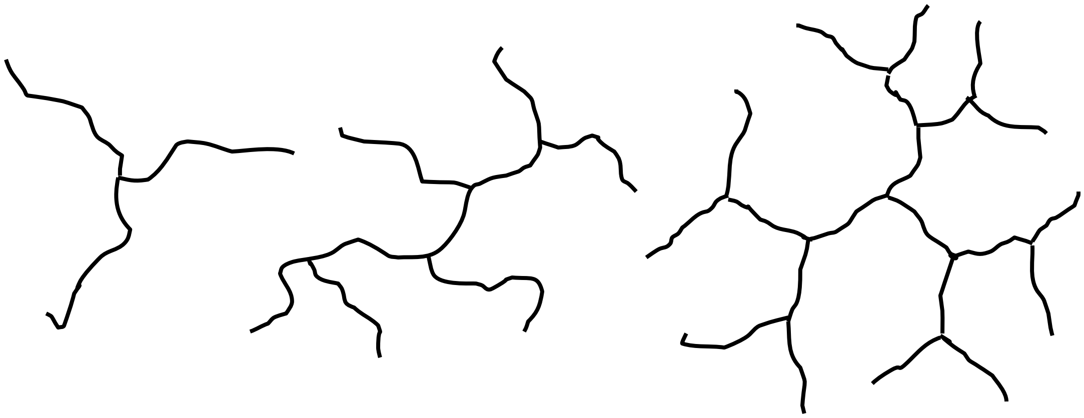
$$P_{AB}(Q) = F_A(Q) F_B(Q)$$

$$P_{BC}(Q) = F_B(Q) F_C(Q)$$

$$P_{AC}(Q) = F_A(Q) E_B(Q) F_C(Q).$$

The scattering lengths have been omitted for convenience. They have all been assumed to be equal. In order to calculate the SANS scattering cross section, one would have to include the contrast factors, the segment volumes, the polymer macromolecules number densities, and the inter-polymer structure factors.

Other more complex architectures can be handled this way.



Star Polymer Comb Polymer Dendrimer

Figure 7: Various possible polymer architectures exist.

4. STAR POLYMER ARCHITECTURE

The simplest case of polymer chain branching is the star polymer which is considered here.

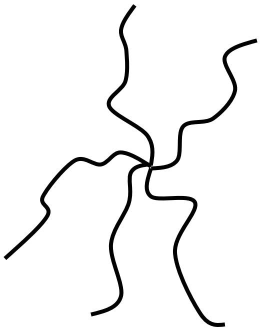


Figure 8: Representation of a star polymer with 5 branches.

The form factor for a star polymer containing n_b branches and n statistical segments per branch is given by:

$$P(Q) = \frac{1}{n_b{}^2 n^2}\left(n_b n^2 P(n) + n_b(n_b - 1)n^2 F^2(n)\right). \tag{22}$$

P(n) is the form factor for a chain with n segments (Debye function) and F(n) is the form factor amplitude. Consider the following relationship (identity):

$$(2n)^2 P(2n) = 2n^2 P(n) + 2n^2 F^2(n). \tag{23}$$

Therefore:

$$P(Q) = \frac{1}{n_b}\left(2P(2n) + (n_b - 2)F^2(n)\right). \tag{24}$$

This is the result for the form factor for a Gaussian polymer star. More complicated architectures (comb, dendrimers, arborescent structures, etc) can be handled this way.

5. POLYMER RINGS

The form factor for a polymer ring can be calculated using a multivariate Gaussian distribution approach. For a Gaussian polymer ring, P(Q) can be calculated as follows:

$$P(Q) = \frac{1}{n^2}\sum_{i,j}^{n} \exp\left[-\frac{Q^2 < r_{ij}{}^2 >}{6}\right]. \tag{25}$$

In order to evaluate $<r_{ij}{}^2>$, construct the ring from a linear chain which is then closed.

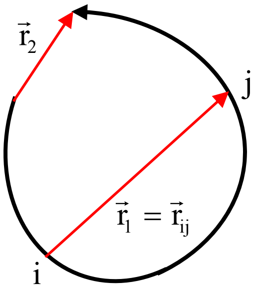


Figure 9: A polymer ring can be constructed by closing a linear chain.

A bivariate Gaussian distribution is defined as:

$$P(\vec{r}_1, \vec{r}_2) = \left(\frac{3}{2\pi a^2}\right)^3 \frac{1}{\Delta}\exp\left(-\frac{3}{2a^2}\sum_{\mu,\nu}^{2} \vec{r}_\mu . D_{\mu\nu} . \vec{r}_\nu\right). \tag{26}$$

Here $\vec{r}_1 = \vec{r}_{ij}$, Δ is the determinant of the correlation matrix $\underline{\underline{C}}$, $\underline{\underline{D}}$ is the inverse ($\underline{\underline{D}} = \underline{\underline{C}}^{-1}$) and the 4 elements of $\underline{\underline{C}}$ are given by: $C_{\mu\nu} = < \vec{r}_\mu . \vec{r}_\nu > / a^2$ with {μ,ν=1,2}. The ring closing step is formed by setting $\vec{r}_2 = 0$. This leaves a univariate Gaussian distribution:

$$P(\vec{r}_1) = \frac{P(\vec{r}_1, 0)}{\int d\vec{r}_1 P(\vec{r}_1, 0)} \tag{27}$$

$$= \left(\frac{3}{2\pi a^2} \right)^{\frac{3}{2}} D_{11}^{\frac{3}{2}} \exp\left(-\frac{3}{2a^2} D_{11} \vec{r}_1^{\,2} \right).$$

The average mean square distance between 2 monomers i and j that belong to the blocks of length n is therefore given by:

$$\frac{< r_{ij}^2 >}{a^2} = \frac{1}{D_{11}}. \tag{28}$$

More specifically, in this case:

$$C_{11} = \frac{< r_1^2 >}{a^2} = (j - i) \tag{29}$$

$$C_{22} = \frac{< r_2^2 >}{a^2} = n.$$

So that:

$$D_{11} = \frac{n}{|i-j| \left(n - |i-j| \right)} \tag{30}$$

$$< r_{ij}^2 > = a^2 \, |i-j| \left(1 - \frac{|i-j|}{n} \right).$$

The form factor for the polymer ring is therefore:

$$P(Q) = \frac{1}{n^2} \sum_{i,j}^{n} \exp\left[-\frac{Q^2 a^2 \, |i-j|}{6} \left(1 - \frac{|i-j|}{n} \right) \right] \tag{31}$$

$$= \frac{1}{n^2}\left\{ n + 2n\sum_{k=1}^{n}\left(1-\frac{k}{n}\right)\exp\left[-\frac{Q^2a^2k}{6}\left(1-\frac{k}{n}\right)\right]\right\}.$$

The first term is dropped for n >>1. In order to simplify this equation, we take the continuous chain limit (whereby $Q^2a^2/6<<1$ and n >>1 but keeping $Q^2a^2n/6$ finite) and change the summations into integrations:

$$P(Q) = 2\int_0^1 ds(1-s)\exp\left[-\frac{Q^2a^2n}{6}s(1-s)\right]. \qquad (32)$$

We notice the following identity:

$$2\int_0^1 ds(1-s)\exp\left[-\frac{Q^2a^2n}{6}s(1-s)\right] = \int_0^1 ds\exp\left[-\frac{Q^2a^2n}{6}s(1-s)\right]. \qquad (33)$$

Therefore:

$$P(Q) = \int_0^1 ds\exp\left[-\frac{Q^2a^2n}{6}s(1-s)\right]. \qquad (34)$$

After integration variable changes and a few manipulations, one obtains the final result:

$$P(Q) = \frac{D(U)}{U}. \qquad (35)$$

Here D(U) is Dawson's integral:

$$D(U) = \exp\left(-U^2\right)\int_0^U dt\exp\left(t^2\right). \qquad (36)$$

The variable U is given by $U = \sqrt{Q^2a^2n/6}/2 = QR_g/2$.

The method described here for a single ring can be generalized to calculate more complex structures containing looping features.

6. MORE COMPLEX RING-CONTAINING ARCHITECTURES

Another case involving correlations between 2 blocks (n monomers each) separated by 3 linear chain portions (n_1, n_2 and n_3 monomers respectively) that are joined at the extremities of the 2 blocks is considered here. This structure can be constructed using a long linear chain (with $2n+n_1+n_2+n_3$ monomers) that includes 2 crosslinks (corresponding to $\vec{r}_2 = 0$ and $\vec{r}_3 = 0$). All segment lengths are assumed to be equal to a for simplicity.

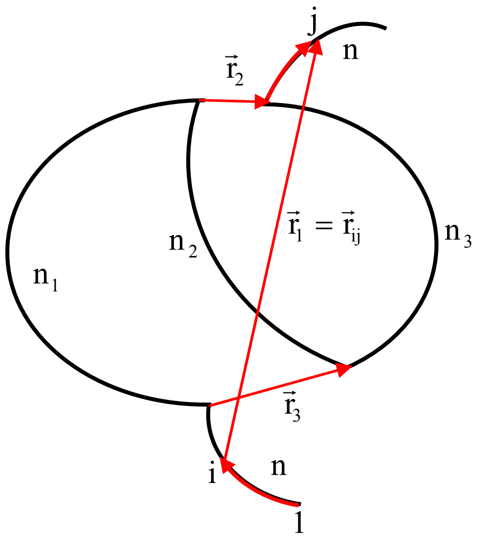


Figure 10: Correlations between two (outer) blocks for a particular polymer chain architecture.

A trivariate Gaussian distribution describing this structure is given by:

$$P(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \left(\frac{3}{2\pi a^2}\right)^{\frac{9}{2}} \frac{1}{\Delta^{\frac{3}{2}}} \exp\left(-\frac{3}{2a^2}\sum_{\mu,\nu}^{3} \vec{r}_\mu . D_{\mu\nu} . \vec{r}_\nu\right). \tag{37}$$

Here also $\vec{r}_1 = \vec{r}_{ij}$ and $\underline{\underline{C}}$ has 9 elements. The two crosslinks are formed by setting $\vec{r}_2 = \vec{r}_3 = 0$ leading to $P(\vec{r}_1)$.

In this case:

$$\begin{aligned}
C_{11} &= (n\text{-}i\text{+}j\text{+}n_1\text{+}n_2\text{+}n_3) \\
C_{12} &= C_{21} = (n_2+n_3) \\
C_{13} &= C_{31} = (n_1+n_2) \\
C_{22} &= (n_2+n_3) \\
C_{23} &= C_{32} = n_2 \\
C_{33} &= (n_1+n_2).
\end{aligned} \tag{38}$$

Therefore:

$$< r_{ij}{}^2 >= a^2\left[\frac{(-i+j+n)(n_1n_2+n_1n_3+n_2n_3)+n_1n_2n_3}{n_1n_2+n_1n_3+n_2n_3}\right]. \qquad (39)$$

The partial form factor describing correlations between the two outer blocks is given by:

$$P(Q)=\frac{1}{n^2}\sum_{i,j}^{n}\exp\left(-\frac{Q^2<r_{ij}{}^2>}{6}\right) \qquad (40)$$

which can be written simply as:

$$P(Q)=\exp\left[-\frac{Q^2a^2}{6}\left(\frac{1}{n_1}+\frac{1}{n_2}+\frac{1}{n_3}\right)\right]\frac{\left[1-\exp(-Q^2a^2n/6)\right]^2}{\left[Q^2a^2n/6\right]^2}. \qquad (41)$$

In summary, this method consists in forming the correlation diagram using one single chain and choosing judiciously the location of crosslinks. All elements of the correlation matrix $\underline{\underline{C}}$ need to be calculated so that the first element (recall that $\vec{r}_1=\vec{r}_{ij}$) of its inverse, $D_{11}=\Delta_{11}/\Delta$ (where Δ_{11} is the cofactor of element C_{11} and Δ is the determinant of $\underline{\underline{C}}$) is obtained therefore yielding $<r_{ij}{}^2>/a^2=\Delta/\Delta_{11}$. This procedure is useful for the calculation of correlations needed in the modeling of more complicated architectures ("olympic rings", regular networks, etc).

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QUESTIONS

1. What is the form factor for a Gaussian polymer coil of radius of gyration R_g?
2. Calculate the form factor $P_{AC}(Q)$ between the two outer blocks for a triblock copolymer A-B-C.
3. What is the form factor for a Gaussian polymer ring?
4. Calculate the radius of gyration for a Gaussian ring polymer.

ANSWERS

1. The form factor for a Gaussian polymer coil is given by the Debye function $P(Q) = 2\left[\exp\left(-Q^2 R_g{}^2\right) - 1 + Q^2 R_g{}^2\right] / Q^4 R_g{}^4$ where R_g is the radius of gyration.
2. The form factor $P_{AC}(Q)$ between the two outer blocks for a triblock copolymer A-B-C is given by $P_{AC}(Q) = \dfrac{1 - \exp\left[-Q^2 R_{gA}{}^2\right]}{Q^2 R_{gA}{}^2} \dfrac{\exp\left[-Q^2 R_{gB}{}^2\right]}{Q^2 R_{gB}{}^2} \dfrac{1 - \exp\left[-Q^2 R_{gC}{}^2\right]}{Q^2 R_{gC}{}^2}$ where R_g's are the radii of gyration of the blocks.
3. The form factor for a Gaussian polymer ring is given by $P(Q) = \left\{\exp\left(-U^2\right)/U\right\} \int_0^U dt \exp\left(t^2\right)$ where $U = R_g/2$.
4. The radius of gyration squared for a Gaussian ring polymer is given by:

$$R_g{}^2 = na^2 \int_0^1 ds\, s(1-s)^2 = na^2 \int_0^1 ds\, (s - 2s^2 + s^3) = na^2 \left[\frac{s^2}{2} - 2\frac{s^3}{3} + \frac{s^4}{4}\right]_0^1 = \frac{na^2}{12} = \frac{1}{2}\frac{na^2}{6}.$$

Recall that for a linear polymer $R_g{}^2 = \dfrac{na^2}{6}$. Here n is the degree of polymerization and a is the statistical segment length.