Theoretical Model

For semiflexible dendrimers the correlation between bond vectors is expressed through the generalized potential V_s in the framework of optimized Rouse-Zimm approach

$$V_s(\boldsymbol{l}_i) = \frac{K}{2} \sum_i U_{ij} \boldsymbol{l}_i \cdot \boldsymbol{l}_j \tag{1}$$

where k_B is Boltzmann constant, $K = 3k_B T/l^2$ is spring constant and $\boldsymbol{l}$ bond vector which is expressed as $\boldsymbol{l}_i = \boldsymbol{R}_i - \boldsymbol{R}_j$. Alternatively the bond vector may be expressed in terms of incidence matrix $\boldsymbol{G}$ as $\boldsymbol{l}_i = \sum_k \boldsymbol{G}^T_{ik} \boldsymbol{R}_k$. On using this definition we can rewrite eqn. 1

$$V_s(\boldsymbol{R}_i) = \frac{K}{2} \sum_i \left(\boldsymbol{G} \cdot \boldsymbol{U} \cdot \boldsymbol{G}^T\right)_{ij} \boldsymbol{R}_i \cdot \boldsymbol{R}_j \tag{2}$$

Here the structure of dendrimers is represented through the connectivity matrix $[\boldsymbol{A}] = \left[\boldsymbol{G} \cdot \boldsymbol{U} \cdot \boldsymbol{G}^T\right]$, where the elements of $N \times (N-1)$ incidence matrix, G_{ij} are: $G_{ij} = -1$ if the bond vector, $\boldsymbol{l}_j$ starts at i-th bead, $G_{ij} = +1$ if bond vector $\boldsymbol{l}_j$ points to i-th bead, and $G_{ij} = 0$ otherwise. Semiflexibility is incorporated through the $(N-1) \times (N-1)$ bond correlation matrix $\boldsymbol{U}$ in Eq. 3, whose elements contain the average scalar product of bond vectors and defined as

$$\left[U^{-1}\right]_{ij} = \frac{\langle \boldsymbol{l}_i \cdot \boldsymbol{l}_j \rangle}{l^2} \tag{3}$$

The average scalar product of bond vectors, $\langle \boldsymbol{l}_i \cdot \boldsymbol{l}_j \rangle$ has been modeled through the normalized spherical harmonics $Y_l^m(\theta, \phi)$, which incorporate the effect of both direction and orientation of respective bond vectors through angles θ and ϕ respectively. In the spherical harmonics approach the average scalar product of bond vectors is defined as

$$\begin{aligned} \frac{\langle \boldsymbol{l}_i \cdot \boldsymbol{l}_j \rangle}{l^2} &= \pm Y_l^m(\theta, \phi) \\ &= \pm \sqrt{3/4\pi}\ \sin\theta\ \cos\phi \end{aligned} \tag{4}$$

The plus sign denotes for head to tail arrangement of adjacent bonds and the minus sign otherwise. For the non-adjacent bonds, i and k, the shortest topological distance is given by

$$\langle \boldsymbol{l}_i \cdot \boldsymbol{l}_k \rangle = \langle \boldsymbol{l}_i \cdot \boldsymbol{l}_{j_1} \rangle \cdot \langle \boldsymbol{l}_{j_1} \cdot \boldsymbol{l}_{j_2} \rangle \ldots \langle \boldsymbol{l}_{j_n} \cdot \boldsymbol{l}_k \rangle\, l^{-2n} \tag{5}$$

where $(j_1, j_2, \ldots j_n)$ denotes the unique shortest distance between the i-th and k-th bond vectors. From Eq.4, degree of semiflexibility is a function of the bond orientation angle,

ϕ except the case of $\phi = 0$ which corresponds to the freely rotating model. The values of ϕ lie between the range $(0, \pi)$, in which ranges between $(0, \pi/2)$ and $(\pi/2, \pi)$ represent the conformation and expanded conformations of dendrimers respectively. The angle between adjacent bond vectors, θ, can take any values between 0 to π and the range of this correlation depends on the functionality of branch point of dendrimer, such that $cos\ \theta \in [0, 1/(f_i - 1)]$. Dendrimer shows different type of structure behavior in compressed (i.e. $\phi \in (0, \pi/2)$) and expanded (i.e. $\phi \in (\pi/2, \pi)$) zones.