

Supporting information for: Topological defects and shape of aromatic self-assembled vesicles

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1 Point groups for 6T and 5T

In Figure 1a we show two aromatic molecules (6T and 5T) with even and odd number of thiophene cores and the corresponding symmetry operations, which transform the molecule into itself. For two-dimensional rectangular lattice, like the one enclosing 6T and 5T molecules, the possible symmetry operations are mirror-reflections across line, denoted by m . For 6T molecule, we can write the following symmetry operations which leave one point unmoved¹

$$m_z = \begin{pmatrix} 1 & & \\ & 1 & \\ & & -1 \end{pmatrix} \quad \text{and} \quad 2_z = m_x m_y = \begin{pmatrix} -1 & & \\ & -1 & \\ & & 1 \end{pmatrix}. \quad (1)$$

Their product $m_x m_y m_z = \begin{pmatrix} -1 & & \\ & -1 & \\ & & -1 \end{pmatrix}$, acting on a vector, results in the total inversion symmetry. For 5T molecule the point group is different, containing the operators

$$m_z = \begin{pmatrix} 1 & & \\ & 1 & \\ & & -1 \end{pmatrix}, \quad m_y = \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}, \quad m_x = m_y m_z = \begin{pmatrix} 1 & & \\ & -1 & \\ & & -1 \end{pmatrix}. \quad (2)$$

These symmetry operations leave vector $v = (x, 0, 0)$ invariant, which is not the case for 6T molecules. This result can be generalized to even and odd number of thiophene and benzene rings.

2 Conformal mapping

Let us consider a spheroid, which is a surface of revolution given by the following parametrization

$$\mathbf{x}(u, v) = (a \sin v \cos u, a \sin v \sin u, c \cos v), \quad 0 \leq v \leq \pi, \quad 0 \leq u \leq 2\pi, \quad (3)$$

with semiaxes c and a (see Figure 1d). Then, the metric of spheroid is given by

$$ds_1^2 = (a^2 \cos^2 v + c^2 \sin^2 v) dv^2 + a^2 \sin^2 v du^2. \quad (4)$$

The mapping of spheroids onto a sphere with metric $ds^2 = R^2(d\theta^2 + \sin^2 \theta d\phi^2)$ is said to be conformal if we can write

$$ds^2 = e^{2\lambda(\mathbf{u})} ds_1^2, \quad (5)$$

where $e^{2\lambda(\mathbf{u})}$ is called the conformal factor, which varies with position $\mathbf{u} = \{u, v\}$ on spheroid. Because of the rotational symmetry $u = \phi$ and conformal factor depends only on parameter v . By

equating two metrics we find that

$$e^{2\lambda(v)} = \frac{R^2 \sin^2 \theta}{a^2 \sin^2 v}, \quad \frac{d\theta}{\sin \theta} = \pm dv \sqrt{\cot^2 v + \frac{c^2}{a^2}}. \quad (6)$$

By integrating both sides of the second equality we get

$$\log \left(\tan \frac{\theta}{2} \right) = g(v) \equiv -\sqrt{-1 + \eta^2} \arctan \left(\frac{\sqrt{-1 + \eta^2} \cot v}{\sqrt{\eta^2 + \cot^2 v}} \right) - \log (\cot v + \sqrt{\eta^2 + \cot^2 v}), \quad (7)$$

where $\eta = c/a$. Substituting $\sin \theta = 2 \tan(\theta/2)/(1 + \tan^2 \theta/2)$ into Eq. (6) we find the analytical expression for the conformal factor

$$e^{2\lambda(v)} = \frac{R^2}{a^2 \sin^2 v \cosh^2 g(v)}, \quad (8)$$

and the limit of interest

$$\lim_{v \rightarrow 0} \lambda(v) = \log \frac{R}{a} - \sqrt{-1 + \eta^2} \arctan \sqrt{-1 + \eta^2}. \quad (9)$$

3 Free energy

3.1 Contribution from defects

The pair Green function for topological defects on deformed sphere can be defined similar as for superfluids in reference²

$$\Gamma(\mathbf{x}_i, \mathbf{x}_j) = -\frac{1}{2\pi} \log \frac{\mathcal{D}_{ij}}{d} + \frac{1}{4\pi} (\lambda(\mathbf{x}_i) + \lambda(\mathbf{x}_j)), \quad (10)$$

where \mathcal{D}_{ij} is the distance between two defects on the sphere (the chord between two points!) and d is the core size of the defect.³ This representation of the Green function already includes both the interaction between defects (first term) and the position dependent self-energy of defect. In the

case of two topological defects on sphere with topological charge $q_i = q_j = +1$, the minimum of $F_{\text{defect}} = 4\pi^2 K_A q_i q_j \Gamma(\mathbf{x}_i, \mathbf{x}_j)$ corresponds to the defects located at the north N ($v = 0$) and the south S ($v = \pi$) poles (see Figure 1d). It gives $\mathcal{D}_{ij} = 2R$, and together with Eqs. (9) and (10) we find the Green function

$$\Gamma(0, \pi) = -\frac{1}{2\pi} \left(\log \frac{2a}{d} + \sqrt{-1 + \eta^2} \arctan \sqrt{-1 + \eta^2} \right), \quad (11)$$

and consequently an analytical expression for F_{defect} . In Figure Figure 1 below we plot the Green function $\Gamma(0, \pi)$ and the Gaussian curvature K as the function of η . As was expected, the Green function decreases with η , while the Gaussian curvature is increasing, resulting in the more negative $\Gamma(0, \pi)$ and thus F_{defect} for higher K , which is in agreement with a theory.⁴

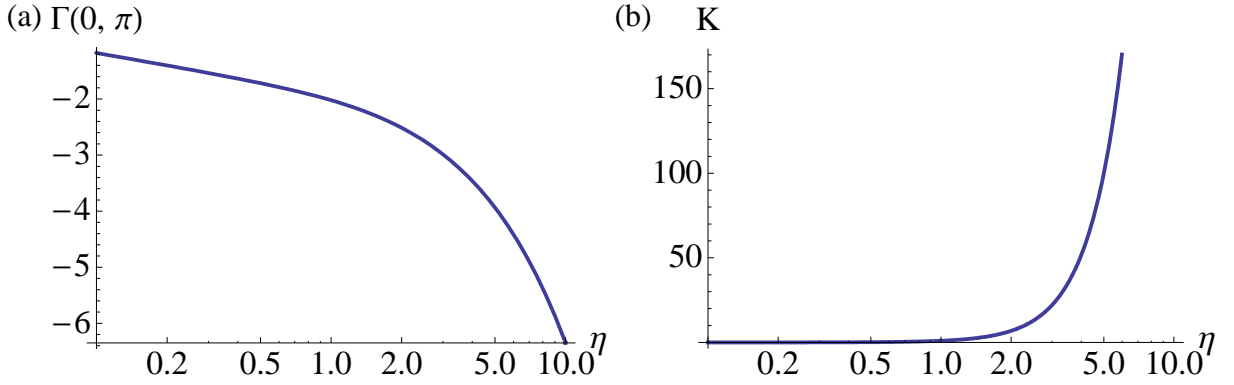


Figure 1: (a) The Green function $\Gamma(0, \pi)$ given by Eq. (11). For this plot we choose the equilibrium radius of the vesicle $R = 100$ nm and the size of the core $d = 3.5$ Å as the equilibrium distance between thiophene cores. (b) The Gaussian curvature $K = c^2/a^4 = \eta^2/a^2$ calculated at the poles, assuming the condition of constant surface (Eq. 16).

3.2 Bending energy

The bending energy proposed by Helfrich in⁵ is written as

$$F_{\text{bend}} = 2k \iint dS H^2, \quad (12)$$

where H is the mean curvature and the integral is over the surface S . For spheroids (Eq. 3)

$$dS = a \sin v \sqrt{a^2 \cos^2 v + c^2 \sin^2 v} du dv, \quad (13)$$

$$H = \frac{1}{2} \left(\frac{c/a}{\sqrt{a^2 \cos^2 v + c^2 \sin^2 v}} + \frac{ac}{(a^2 \cos^2 v + c^2 \sin^2 v)^{3/2}} \right). \quad (14)$$

After some calculations, the integral in Eq. (12) can be simplified to the following form

$$F_{\text{bend}} = 2k\pi\eta^2 \left\{ \frac{\tanh^{-1} \sqrt{1-\eta^2}}{\sqrt{1-\eta^2}} + \frac{2}{\eta^2} + \frac{1}{3\eta^2} \left(1 + \frac{2}{\eta^2} \right) \right\}. \quad (15)$$

This energy term does not depend on the size of the vesicle only on the dimensionless parameter η .

However, the Green function in Eq. (11) depends on the absolute value of the distance between the defects, therefore in all our calculations we assumed the condition of constant surface of spheroid

$$S = 2\pi a^2 \left(1 + \eta^2 \frac{\tanh^{-1} \sqrt{1-\eta^2}}{\sqrt{1-\eta^2}} \right) = \text{const}, \quad (16)$$

yielding constant density of the molecules.

4 Estimate of the ratio of K_A/k

We assume that for aromatic molecules this value is mainly determined by the long-ranged π - π interactions between aromatic rings, and not by extrinsic effect (e.g. solvent) as discussed in⁶ for thiophene oligomers. Therefore, we propose to estimate the ratio K_A/k by using the results of quantum chemistry calculations for the binding energy of thiophene dimers with different relative orientations.⁷ The basic idea is to associate the energy of the splay configuration of two N -thiophene molecules with the value of the bending rigidity k (see Figure Figure 2b below), and the value of hexatic constant K_A with the rotation around the long axes of the molecule (see Figure Figure 2c below). Then, based on the calculated interaction energy for different geometries of thiophene dimers (configurations A , G , H of Figure 2, Table 2 of refer-

ence⁷⁾ we find $k \propto E_{\text{total}}(G) - E_{\text{total}}(A) = -2.05 - (-1.32) = -0.73 \text{ kcal/mol} \approx 5 \cdot 10^{-21} \text{ J}$ and $K_A \propto E_{\text{total}}(H) - E_{\text{total}}(A) = -2.28 - (-1.32) = -0.96 \text{ kcal/mol}$, yielding $K_A/k \approx 1.3$.

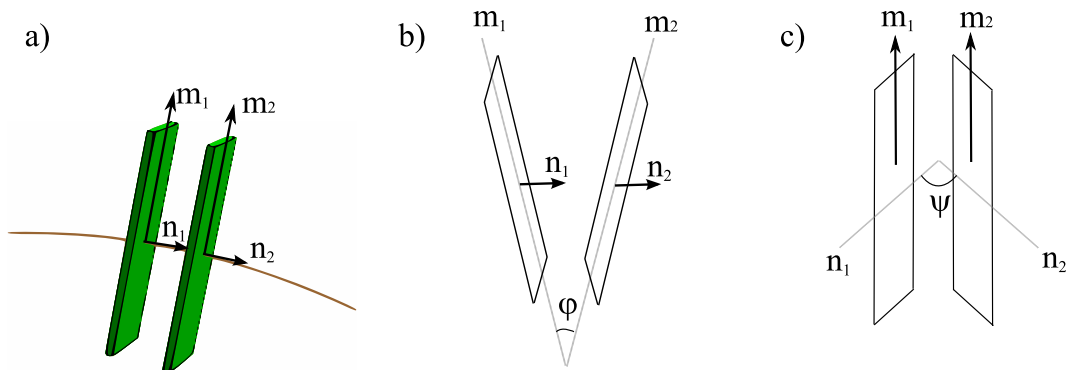


Figure 2: (a) Flat plaquettes, described by unit vectors n_i and m_i , which are normal and tangent vectors to the surface respectively. (b) The splay configuration of two plaquettes with the angle ϕ defined as $\cos \phi = (\mathbf{m}_1, \mathbf{m}_2)$. (c) The rotation around the long axes of two plaquettes with the angle ψ defined as $\cos \psi = (\mathbf{n}_1, \mathbf{n}_2)$.

Notes and References

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