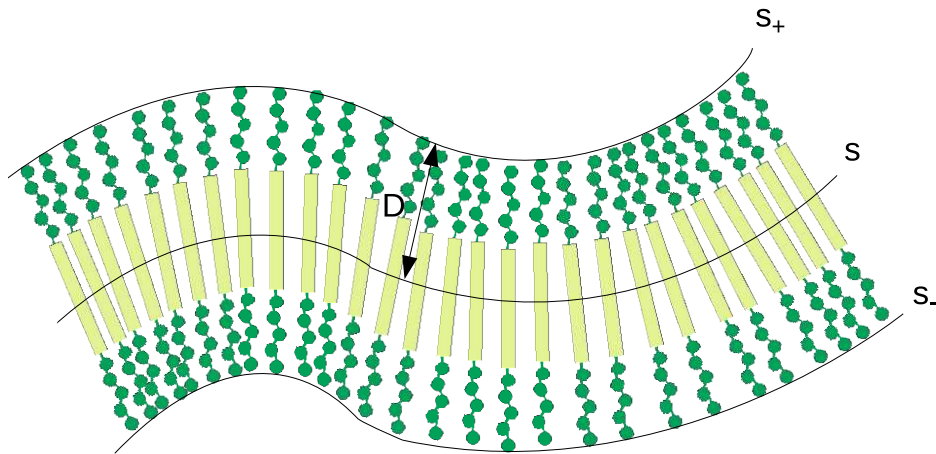


Curvature of Self-Assembled Membranes

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Theory of Condensed Matter

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Amphiphilic molecules can self-assemble to molecular membranes. These membranes can appear in different shapes, such as vesicles and cylinders, with a radius much bigger than the length of the molecules.

Self-assembled structures are of general interest in nanotechnology, but already the fact that molecules structure spontaneously is intriguing!

In this report we will investigate the contribution of the solvent-tail interactions to the free energy and their influence on the equilibrium shapes of the membranes.

There will be two starting points for this investigation: on the one hand we will start from the microscopic Flory–Huggins model to calculate the free energy of mixing. On the other hand we will assume a macroscopic approach of the geometry, shape and curvature of the membranes as two-dimensional surfaces.

Special attention will be paid to the length of the molecules.

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1 Introduction

A spectacular feature of amphiphilic molecules is their ability to self-assemble. Spontaneously they organize themselves into well-ordered structures, such as vesicles and cylinders.

Self-assembly is a general phenomenon seen in biological systems, such as cell membranes and used in nanotechnology to get the desired structures, which are programmed in the shapes and characteristics of the molecules. A better understanding of self-assembly could lead to various possible applications in material science, relevant for pharmacology, catalysis and other fields. But also to a better understanding of biological systems, such as cell membranes and other biological matter. With this report I would like to give a small contribution to the research in the field of molecular self-assembly.

The motivation for this investigation, lies in the experimental data reported in Refs. [3] and [10]. The amphiphilic molecules used are sexithiophene (6T molecules) in different solvents and, with different results: vesicles and cylinders were formed! In Ref. [6] an idea is proposed to calculate the contribution of the tail-solvent interactions. I will work out this idea, for variable length of the molecules and calculate the magnitude of the contribution.

In chapter 2 I will remind what self-assemblies are, which molecules and solvents are used and I will question the influence of the length of the molecules on the equilibrium structure and shape of the membranes. Following the ideas of Ref. [6], I will start in chapter 3 with the Flory–Huggins model, to calculate the free energy of mixing in terms of the concentrations and length of the molecules of the 6T-tails and the solvent. The definitions and mathematical background of curvature will be described in chapter 4. Furthermore we will look at transferred curved surfaces and express the surface of the interface of the tails with the solvent in the curvature and the surface of the cores. In chapter 5 we will remember the Landau Ginzburg Hamiltonian, which we will use in chapter 6, together with the results of chapter 3 and 4, to get the free energy of mixing in terms of the concentrations, the length of the molecules and the curvature. From this we can draw our conclusions about the influence of the molecular length on the equilibrium structures and shapes of the membranes. The behavior and magnitude of the contribution of the tail-solvent interactions will be calculated in chapter 7 and reported in chapter 8.

2 Molecular Self-assembled Membranes

2.1 Self-assembling

A spectacular property of soft matter is that it can self-assemble Ref.[1]: molecules can arrange themselves to supra-molecular structures. But what is the difference between this soft-condensed matter and crystal structures? The binding energies of this supra-molecular structures are of the order $k_B T$, which is much less than in crystals, where atoms are covalently bonded. The other essential difference between crystal order and self-assembled structures is that crystals are far more ordered. Thermal fluctuations will be more important in self-assembled structures.

The most common examples of self-assembling molecules are amphiphilic molecules, such as soap-molecules. The particular property of these molecules, when put in a solvent, is that they have a part which has affinity with the solvent and they have a part which is repelled by the solvent. In the case of soap, this solvent could be water and the part attracted by the water is called hydrophilic ($\phi\iota\lambda\iota\alpha$ is an ancient Greek word for love, friendship and affection), whereas the part repelled by water is called hydrophobic ($\phi\omicron\beta\omicron\varsigma$, an ancient Greek word for fear).

The solventphobic parts tend to stick together, they will self-assemble. In this way the molecules could arrange themselves, in order to keep the solventphobic parts away from the solvent.

Although it is entropically unfavorable to self-assemble (which mean to be ordered), it is energetically favorable for the solventphobic parts to be next to each-other. A measure for the equilibrium between these two contributions (energetic and entropic) is given by the Helmholtz free energy, which will be calculated in chapter 3.

2.2 Molecule and Solvent

The motivation for this investigation lies in the experimental data reported in Refs. [3] and [10]. The amphiphilic molecules used are sexithiophene (6T molecules), see figure 1. The core of the molecule, denoted in yellow in the schematic representation of the molecule in the figure, is rigid, whereas the tails (denoted in green) are flexible.

The assembly has been studied in different solvents: ethanol, isopropanol, butanol, pentanol, octanol and decanol, which are illustrated in figure 2. These are all polymers consisting of several CH_2 groups and one COH group.

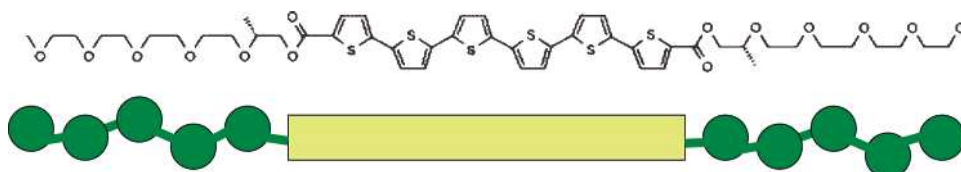
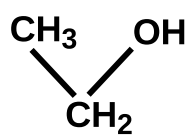


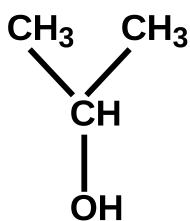
Figure 1: *The amphiphilic molecule, with two solventphilyc tails (green) and a solventphobic core (yellow).*

2.3 Questions

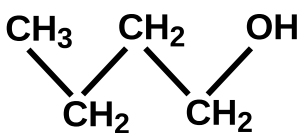
These 6T molecules can either self-assemble or not, depending on the solvents used. If they self-assemble, all cores will line up, like in figure 3. I would expect that, since the tails are identical on both sides of the core, they would assemble into more or less flat membranes. However from the



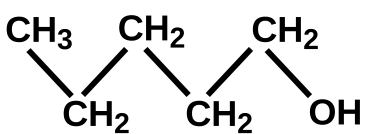
Ethanol



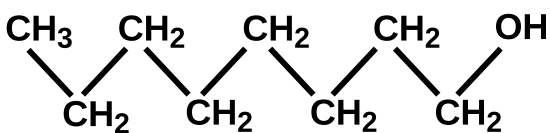
Isopropanol



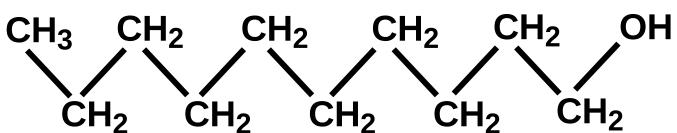
Butanol



Pentanol



Octanol



Decanol

Figure 2: *The different solvents*

optical measurements of Refs. [10] and [3], we know that spheres and cylinders can be formed. One explanation is that it is energetically advantageous for the cores to have no edges where the cores are in contact with the solvent. A closed structure like a sphere, leaves no cores in contact with the solvent. Other possible explanations are that it could be entropically favorable for the tails to be bent, see figure 4. Moreover it could be an energetic advantage for the tails to be further from each other, while they are solventphobic. It means that it is energetically an advantage for a tail molecule to be next to a solvent molecule. The central question in this report is: what is the influence of the length of the molecules (both

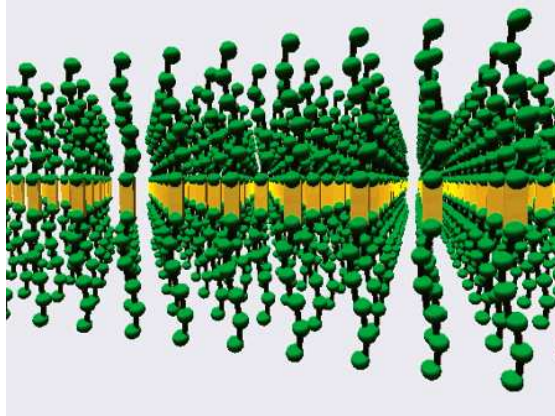


Figure 3: *Schematic drawing of a membrane formed by self-assembled 6T molecules (from Ref.[6]).*

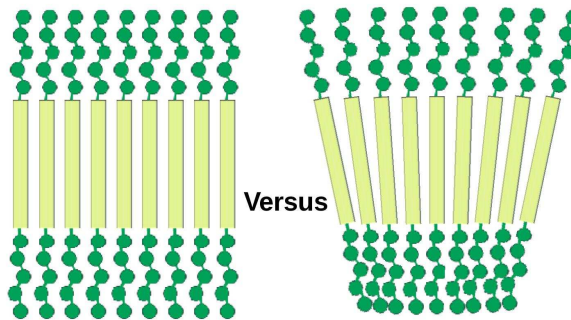


Figure 4: *In this schematic view of a curved membrane one can see that the tails on the upper side have more space, which means that it is entropically more advantageous. At the lower side the tails have less space, which is a disadvantage. But could the advantage be bigger than the disadvantage?*

of the tails and of the solvent) on the curvature and equilibrium shape of the membranes. In Ref. [6] this question is investigated but only for a variable length of the tails. In this report I will expand this investigation to a variable length of the solvent molecules as well.

3 Flory–Huggins Model

To answer the question why molecules would self-assemble or not, we have to look at the change in entropy and the change in energy due to the fact that the molecules are not mixed anymore. Systems favor the highest entropy, which means that systems favor the mixed state. But systems also favor the lowest energy. And if the lowest energy state is the unmixed one, then we have to look for an equilibrium between the tendency to the highest entropy and the (probably opposite) tendency to the lowest energy. A measure for this equilibrium is the free-energy. In experiments normally the pressure is hold constant, which would mean one have to use the Gibbs free energy as thermodynamic quantity to find the equilibrium of the system. In the Flory-Huggins model however, we assume the volume constant, so we use the Helmholtz free energy.

$$\Delta F = \Delta U - T\Delta S \quad (1)$$

To evaluate the change in the free energy (ΔF) we need to calculate the change in entropy (ΔS) and in energy (ΔU) due to mixing. To find this we can use the Flory-Huggins model Ref. [8]. Consider a mixture of two species, named S and T. The idea of this model is to define a small volume v and divide the molecules S in p times this volume v and the molecules T in r times this volume. The total volume of mixing is divided in a lattice with volume elements v too. Dividing everything in certain units, makes the problem discrete, which simplifies it dramatically. The total volumes is considered to be constant in this model. When there are in the total volume n_S S molecules and n_T T molecules, the volume-fraction of S and T monomers are:

$$\begin{aligned} \phi_S &= \frac{(pn_S)v}{(pn_S + rn_T)v} = \frac{pn_S}{pn_S + rn_T} \\ \phi_T &= 1 - \phi_S = \frac{(rn_T)v}{(pn_S + rn_T)v} = \frac{rn_T}{pn_S + rn_T} \end{aligned} \quad (2)$$

3.1 Entropy

To calculate the entropy of mixing, one can use Boltzmann's formula:

$$S = k_B \ln \Omega \quad (3)$$

The number of possible states (Ω) is easily calculated with the lattice model. We have divided the total volume of mixing in a lattice with $N = pn_S + rn_T$ sites. So, for one S molecule there are $N = pn_S + rn_T$ possible positions for its center of mass. In this calculation only the translational entropy is taken in account. This means that we assume that the configurational entropy of the polymers is the same in mixed and unmixed state.

Before mixing, the total number of lattice sites for the S molecules was pn_S . When we calculate now the difference in entropy, due to mixing for one S molecule using formula (3), we find:

$$\Delta S_{\text{of one } S \text{ molecule}} = k_B [\ln (pn_S + rn_T) - \ln (pn_S)] = -k_B \ln \left(\frac{pn_S}{pn_S + rn_T} \right)$$

For all S molecules, the total entropy of mixing of the S molecules becomes:

$$\Delta S_S = -k_B n_S \ln \left(\frac{pn_S}{pn_S + rn_T} \right)$$

When the same calculation is done for the T molecules, we can add the changes in entropy of the S and T molecules and we find the total change in entropy due to mixing:

$$\Delta S_{\text{total}} = \Delta S_S + \Delta S_T = -k_B \left[n_S \ln \left(\frac{pn_S}{pn_S + rn_T} \right) + n_T \ln \left(\frac{rn_T}{pn_S + rn_T} \right) \right] \stackrel{\text{Eq.(2)}}{=} -k_B [n_S \ln \phi_S + n_T \ln \phi_T] \quad (4)$$

There are three different kinds of mixtures:

- **Regular solutions:** both molecules S and T consist of just one monomer $\Rightarrow p = 1$ and $r = 1$.
- **Polymer solutions:** a polymer consisting of $r = N$ monomers in a solvent consisting of single ($p = 1$) monomers.
- **Polymer blends:** two polymers consisting of $p = N_1$ and $r = N_2$ monomers.

Ideal mixtures (mixtures without energetic contribution) are always homogeneous, since the entropic contribution is always positive.

In figure 5 one can see the difference in change in entropy per lattice site. The bottom curve is the regular solution. The top curve is a polymer-blend consisting of two polymers of the same length. The minimum is for equal concentrations of both polymers. The middle curve is the polymer solutions. Here the minimum is for a polymer concentration which is bigger than the solution concentration.

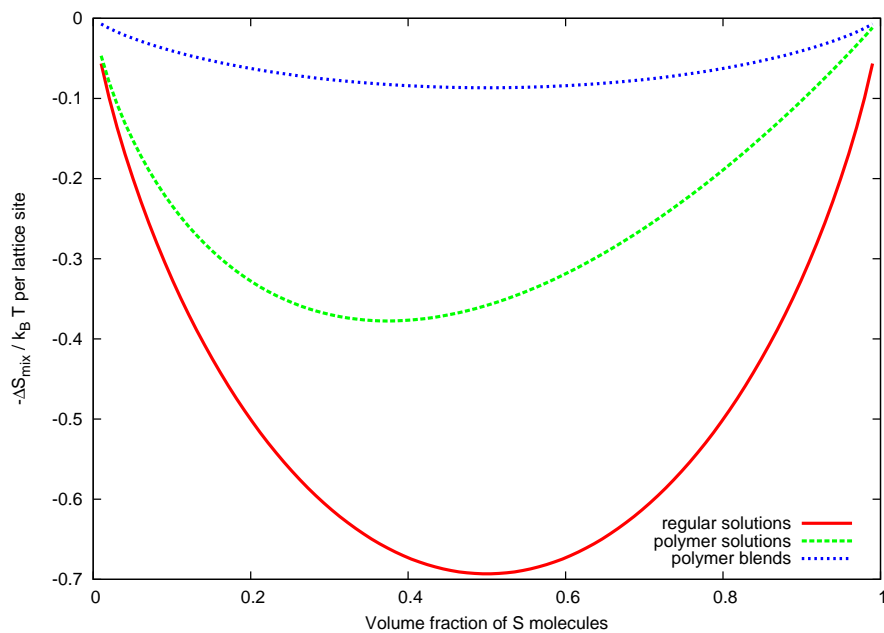


Figure 5: *Entropy of mixing for different mixtures.*

3.2 Energy

The interaction between molecules can either be attractive or repulsive. This determines the sign of the energetic term in the free energy. To calculate the energy of mixing, we first need some assumptions:

- For the mixtures the interactions between the monomers are assumed to be small enough, so that they do not affect the random placement of the monomers on the lattice.
- The theory of regular solution moreover assumes that there are no interactions between the monomers of the chains, so that each monomer can be placed randomly on the lattice.
- The monomers of the molecules S and T are assumed to have the same volume v .

In the Flory-Huggins model all monomers are placed randomly on the lattice. If the interaction energy between two S monomers is u_{SS} , the energy between two T monomers is u_{TT} and the energy between one S and one T monomer is u_{ST} , then the average pair wise interaction energy of one S monomer (after mixing) with a neighbor is the weighted sum of the interaction energies. Likewise the interaction energy of one T monomer can be calculated.

$$\begin{aligned} U_S &= \phi_S u_{SS} + \phi_T u_{ST} \\ U_T &= \phi_T u_{TT} + \phi_S u_{ST} \end{aligned} \quad (5)$$

Each lattice site has z nearest neighbors, so the interaction energy of one S monomer with its neighbors is zU_S . When the total number of lattice sites is $N = pn_S + rn_T$, the number of S monomers in the unit volume is $N\phi_S$, then the total interaction energy of all S monomers with their neighbors is $\frac{zN}{2}\phi_S U_S$. The factor $\frac{1}{2}$ is due to the *pair wise* interaction. For the T monomers the interaction energy is $\frac{zN}{2}\phi_T U_T$. Therefore we can write the total interaction energy as:

$$\begin{aligned} U &= \frac{zN}{2}\{U_S\phi_S + U_T\phi_T\} = && \text{with } \phi_S = \phi, \phi_T = 1 - \phi \\ &\stackrel{Eq.(5)}{=} \frac{zN}{2}\{[u_{SS}\phi + u_{ST}(1 - \phi)]\phi + [u_{ST}\phi + u_{TT}(1 - \phi)](1 - \phi)\} = \\ &= \frac{zN}{2}\{u_{SS}\phi^2 + u_{ST}(1 - \phi)\phi + u_{ST}\phi(1 - \phi) + u_{TT}(1 - \phi)^2\} = \\ &= \frac{zN}{2}\{u_{SS}\phi^2 + 2u_{ST}(1 - \phi)\phi + u_{TT}(1 - \phi)^2\} \end{aligned} \quad (6)$$

We are interested in the change in interaction energy due to mixing. So we also need the interaction energy of one S monomer as well as the interaction energy of one T monomer *before* mixing. Since one S monomer before mixing is only in contact with other S monomers, the interaction energy for one S monomer is $\frac{z}{2}u_{SS}$. And the energy before mixing of one T monomer $\frac{z}{2}u_{TT}$. The number of lattice sites of the volume with S monomers is $N\phi_S = pn_S$ and $N(1 - \phi_S)$ for the T monomers. So that the total energy before mixing is: $U_0 = \frac{zN}{2}[\phi u_{SS} + (1 - \phi)u_{TT}]$.

Therefore the change in energy due to mixing becomes:

$$\begin{aligned}
\Delta U_{mix} &= U - U_0 = \\
&\stackrel{Eq.(6)}{=} \frac{zN}{2} [u_{SS}\phi^2 + 2u_{ST}(1-\phi)\phi + u_{TT}(1-\phi)^2 - u_{SS}\phi - u_{TT}(1-\phi)] = \\
&= \frac{zN}{2} [u_{SS}(\phi^2 - \phi) + 2u_{ST}(1-\phi)\phi + u_{TT}(1 - 2\phi + \phi^2 - 1 + \phi)] = \\
&= \frac{zN}{2} [u_{SS}\phi(\phi - 1) + 2u_{ST}(1-\phi)\phi + u_{TT}\phi(\phi - 1)] = \\
&= \frac{zN}{2} \phi(1-\phi)[2u_{ST} - u_{SS} - u_{TT}] = \\
&= \chi\phi(1-\phi)Nk_B T = \Delta U_{mix} \tag{7}
\end{aligned}$$

The dimensionless Flory-interaction-parameter χ is defined to characterize the difference of interaction energies in the mixture:

$$\chi = \frac{z}{2} \frac{2u_{ST} - u_{SS} - u_{TT}}{k_B T} \tag{8}$$

The interaction energies are negative, so if there is a net repulsion between the two species $\Rightarrow |2u_{ST}| < |u_{SS} + u_{TT}| \Rightarrow \chi > 0 \Rightarrow$ the energetic term in the free energy opposes mixing. However when there is a net attraction between the two species $\Rightarrow |2u_{ST}| > |u_{SS} + u_{TT}| \Rightarrow \chi < 0 \Rightarrow$ the energetic term in the free energy favors mixing.

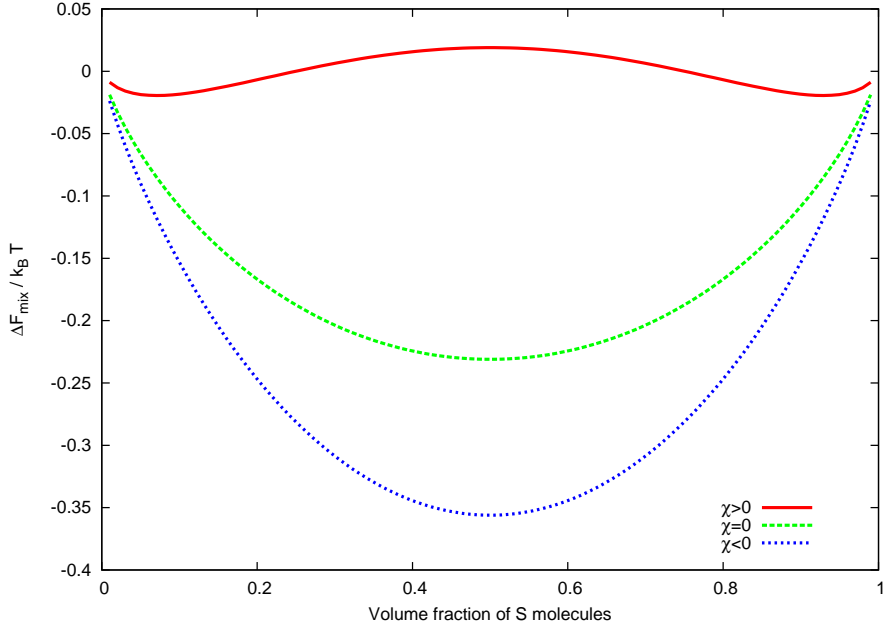


Figure 6: *Free energy of mixing (for regular solutions) for different values of χ*

3.3 Helmholtz Free Energy

To arrive at the Helmholtz free energy, we have to combine Eqs.(1), (4) and (7), to obtain the change in free energy F per lattice site:

$$\begin{aligned}
\Delta F &\stackrel{Eq.(1)}{=} \Delta U - T\Delta S \\
&\stackrel{Eqs.(4),(7)}{=} k_B T [N\chi\phi(1-\phi) + n_S \ln \phi + n_T \ln (1-\phi)] = \\
&\stackrel{Eq.(2)}{=} k_B T [(pn_S + rn_T)\chi \frac{pn_S}{pn_S + rn_T} \frac{rn_T}{pn_S + rn_T} + n_S \ln \frac{pn_S}{pn_S + rn_T} + n_T \ln \frac{rn_T}{pn_S + rn_T}] = \\
&= k_B T [\chi \frac{pn_S rn_T}{pn_S + rn_T} + n_S \ln \frac{pn_S}{pn_S + rn_T} + n_T \ln \frac{rn_T}{pn_S + rn_T}] \tag{9}
\end{aligned}$$

The Flory–Huggins model enabled us to calculate the free energy of mixing in terms of the length of the molecules and the concentration, see Eq.(9).

In figure 6 one can see the difference in free energy of mixing for different values of χ . For ideal mixtures, there is no energetic contribution and only the entropy contributes to the free energy. This is when $\chi = 0$. For most of the mixtures there is an energetic contribution, that can either oppose mixing ($\chi > 0$) or favor mixing ($\chi < 0$). When the energetic contribution opposes mixing, there could occur phase separation.

In this chapter we found, with a simplified model, the free energy of mixing per lattice site, in terms of concentration and molecular lengths. In the following two chapters we will introduce a free energy depending on the curvature, to combine them at last to a free energy which links the length of the molecules and the curvature of the membrane formed by the molecules.

4 Curved Surfaces

To investigate the influence of the length of the molecules on the *shapes* of the membrane, the free energy should not only depend on concentration and molecular length, but also on the curvature of the membranes, since curvature tells something about shape. In this chapter we will define curvature and look at some mathematical background. At last we will express the surface of the interface of the tails and the solvent in terms of the curvature and the surface of the cores.

To classify the shapes of the assembled structures, we assume a geometric point of view. To this purpose we will follow the book of Coxeter (Ref[2], paragraph 17.3 and 19.1-19.4). Do not get frightened from all definitions, equations and formulas, the first goal is to express the normal vectors of the surface, in terms of the derivatives of the position vector as will be given in the Weingarten equations (22).

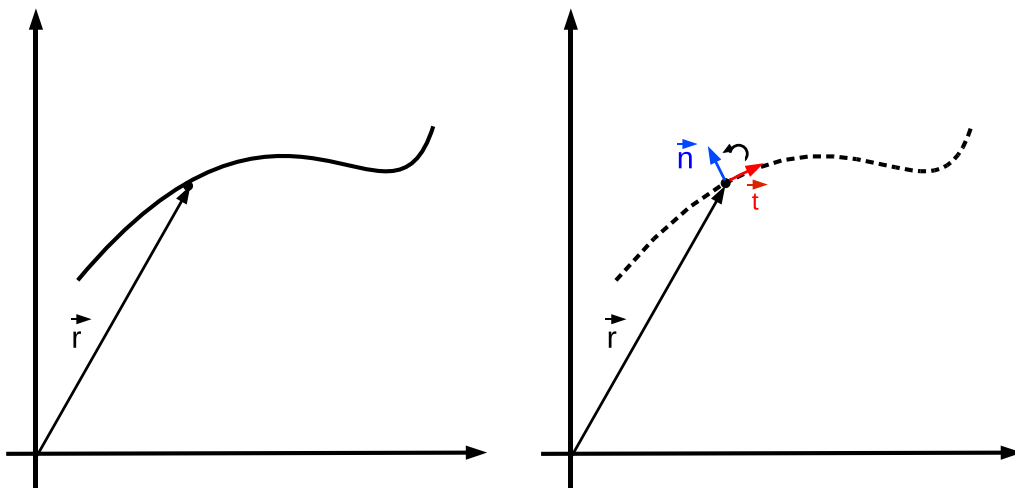


Figure 7: *A two-dimensional curve in space.*

4.1 Curvature

Before starting to derive the Weingarten equations, we first need to define curvature. For this, we take a curve in space. A variable point P on curve is given by vector \vec{r} from the origin. We divide the curve in a sequence of broken lines, see figure 7. The vector along such a segment is $\Delta\vec{r}$. Furthermore s is the arc, measured along the curve from a fixed point A , to a variable point P . Since:

$$\lim \frac{|\Delta\vec{r}|}{\Delta s} = \lim \left[\left(\frac{\Delta x}{\Delta s} \right)^2 + \left(\frac{\Delta y}{\Delta s} \right)^2 + \left(\frac{\Delta z}{\Delta s} \right)^2 \right]^{\frac{1}{2}} = \sqrt{\dot{x}^2 + \dot{y}^2 + \dot{z}^2} = 1$$

the limit of $\frac{\Delta \vec{r}}{\Delta s}$ is the unit tangent vector $\vec{t} = \dot{\vec{r}}$.

For any curve in the x, y -plane, the tangent vector is

$$\vec{t} = (\cos \phi, \sin \phi) \quad (10)$$

where ϕ is the angle that the unit tangent vector \vec{t} makes with the x -axis. The curvature κ of the curve is defined as the arc derivative of this angle:

$$\kappa = \frac{d\phi}{ds} = \dot{\phi}$$

Since \vec{t} is a unit tangent vector, its derivative is perpendicular to it, so in the normal direction, which is derived from \vec{t} with a positive quarter turn (against the rotation of the clock). Thus:

$$\dot{\vec{t}} \stackrel{\text{Eq.(10)}}{=} \frac{d}{ds}(\cos \phi, \sin \phi) = \dot{\phi}(-\sin \phi, \cos \phi) = \kappa \vec{n} \quad (11)$$

We regard κ as positive or negative according to whether \vec{n} is on the concave or convex side of the curve.

We found a suitable definition of the curvature, which we will extend in section 4.3 to curvatures of a surface. For that we will use so-called principal curvatures, whose directions are orthogonal and are called the principal directions.

4.2 Curved Surfaces

Now we will start to derive the Weingarten equations. We will start with describing a surface, the position vector to a certain point on the surface and its derivatives, which are tangents to the surface in the chosen point. From the properties of the unit tangent vectors and their relation to κ we will express the curvature in terms of the derivatives of the position vector. At last we will relate them to the normal and arrive at the Weingarten equations (Eq.(22)).

A surface $f(x, y, z) = 0$ can be represented by a set of parametric equations:

$$x = x(u^1, u^2) \quad y = y(u^1, u^2) \quad z = z(u^1, u^2)$$

We assume that all functions we use are continuous and have all continuous derivatives we need. The vector equation for the surface becomes¹:

$$\vec{r} = \vec{r}(u^1, u^2)$$

A displacement along the tangent to a given curve on the surface, is given by:

$$d\vec{r} = \frac{\partial \vec{r}}{\partial u^1} du^1 + \frac{\partial \vec{r}}{\partial u^2} du^2 = \vec{r}_1 du^1 + \vec{r}_2 du^2 = \sum \vec{r}_i du^i \quad (12)$$

$$\vec{r}_i = \frac{\partial \vec{r}}{\partial u^i} \quad (13)$$

Here we used the subscript i of r_i to denote the partial derivative with respect to u^i .

If u^2 is constant ($u^2 = b$), then $du^2 = 0$, so that $d\vec{r} = \vec{r}_1 du^1$, thus \vec{r}_1 is a tangent vector to this curve. In the same way \vec{r}_2 is another tangent vector to the curve $u^1 = a$. The plane spanned by this two covariant basis vectors is the tangent plane to the surface. We then can define in the same plane the contravariant basisvector \vec{r}^i , which is a normal to the parametric curve.

$$\vec{r}^i \cdot \vec{r}_j = \delta_j^i \quad (14)$$

¹This is like the equation for a curve $\vec{r} = \vec{r}(u^1)$, with the difference that a curve has only one parameter.

In the tangent plane, there are tangent vectors from point (a, b) in all directions. Such vectors can be written in terms of the vectors \vec{r}_i or \vec{r}^i as:

$$\vec{t} = \sum a_i \vec{r}^i = \sum a^i \vec{r}_i \quad (15)$$

Giving for the co- and contra-variant components:

$$a_j = \vec{t} \cdot \vec{r}_j \quad a^j = \vec{t} \cdot \vec{r}^j$$

Since:

$$\vec{t} \cdot \vec{r}_j \stackrel{Eq.(15)}{=} \sum a_i \vec{r}^i \cdot \vec{r}_j \stackrel{Eq.(14)}{=} a_i \delta_j^i = a_j$$

the basis vectors components are:

$$\begin{aligned} \vec{r}_i &= \sum g_{ij} \vec{r}^j & \vec{r}^i &= \sum g^{ij} \vec{r}_j \\ g_{ij} &= \vec{r}_i \cdot \vec{r}_j & g^{ij} &= \vec{r}^i \cdot \vec{r}^j \end{aligned} \quad (16)$$

This implies:

$$\sum \sum g_{hk} g^{ij} = \delta_h^i \delta_k^j \quad (17)$$

When we take the inner-product of \vec{t} in Eq.(15) with itself in various ways, we can rewrite the relation $\vec{t}^2 = 1$ in several ways:

$$\begin{aligned} \vec{t} \cdot \vec{t} &\stackrel{Eq.(15)}{=} \sum a_i \vec{r}^i \cdot \sum a_j \vec{r}^j = \sum \sum a_i a_j \vec{r}^i \cdot \vec{r}^j \stackrel{Eq.(16)}{=} \sum \sum g^{ij} a_i a_j = 1 \\ &= \sum a^i \vec{r}_i \cdot \sum a^j \vec{r}_j = \sum \sum a^i a^j \vec{r}_i \cdot \vec{r}_j \stackrel{Eq.(16)}{=} \sum \sum g_{ij} a^i a^j = 1 \\ &= \sum a^i \vec{r}_i \cdot \sum a_j \vec{r}^j = \sum \sum a^i a_j \vec{r}_i \cdot \vec{r}^j \stackrel{Eq.(14)}{=} \sum a^i a_i = 1 \end{aligned} \quad (18)$$

We now will express the normal \vec{n} in terms of the derivatives of the position vectors \vec{r} . We look at the tangent surface in point P , where there are in all directions tangent vectors, which can be written as in Eq.(15).

To express κ in terms of the vectors \vec{r}_i , we differentiate the unit tangent vector \vec{t} as expressed in Eq.(11), with respect to the arc s :

$$\begin{aligned} \kappa \vec{n} &\stackrel{Eq.(11)}{=} \dot{\vec{t}} \stackrel{Eq.(15)}{=} \frac{d}{ds} \sum a^i \vec{r}_i \\ &= \sum \frac{da^i}{ds} \vec{r}_i + \sum a^i \frac{d\vec{r}_i}{ds} \end{aligned}$$

Multiplying by \vec{n} and remembering that $\vec{n} \perp \vec{r}_i$ gives:

$$\begin{aligned}
\kappa &= \kappa \vec{n} \cdot \vec{n} = \sum a^i \frac{d\vec{r}_i}{ds} \cdot \vec{n} & \text{With } \frac{d}{ds} &= \sum a^j \frac{\partial}{\partial u^j} \\
&= \sum \left(a^i \sum a^j \frac{\partial \vec{r}_i}{\partial u^j} \right) \cdot \vec{n} \\
&\stackrel{\text{Eq.(13)}}{=} \sum \sum a^i a^j \underbrace{\frac{\partial^2 \vec{r}}{\partial u^i \partial u^j}}_{\vec{r}_{ij}} \cdot \vec{n} \\
&= \sum \sum a^i a^j \underbrace{\vec{r}_{ij}}_{b_{ij}} \cdot \vec{n} \\
&= \sum \sum b_{ij} a^i a^j
\end{aligned} \tag{19}$$

One can see that b_{ij} is symmetric in its indices:

$$b_{ij} \stackrel{\text{Eq.(19)}}{=} \vec{r}_{ij} \cdot \vec{n} = \frac{\partial^2 \vec{r}}{\partial u^i \partial u^j} \cdot \vec{n} = \frac{\partial^2 \vec{r}}{\partial u^j \partial u^i} \cdot \vec{n} = b_{ji}$$

From $\vec{r}_i \perp \vec{n} \Rightarrow \vec{r}_i \cdot \vec{n} = 0$ it follows when we differentiate $\vec{r}_i \cdot \vec{n} = 0$ with respect to u^j :

$$\vec{r}_{ij} \cdot \vec{n} + \vec{r}_i \cdot \vec{n}_j = 0 \tag{20}$$

so we can express the coefficients b_{ij} in terms of the derivatives of the normal vector and the position vector.

$$b_{ij} \stackrel{\text{Eq.(19)}}{=} \vec{r}_{ij} \cdot \vec{n} \stackrel{\text{Eq.(20)}}{=} -\vec{r}_i \cdot \vec{n}_j = -\vec{n}_i \cdot \vec{r}_j \tag{21}$$

And so we can define the mixed tensor:

$$b_j^i = \sum g^{ik} b_{ij} = - \sum g^{ik} \vec{r}_i \cdot \vec{n}_j = -\vec{r}^k \cdot \vec{n}_j$$

When we multiply \vec{n}_i , as written in Eq.(21), by \vec{r}^i , we find the derivative of the normal vector expressed in terms of the coefficients b_{ij} and the derivatives of the position vector:

$$\vec{n}_i \cdot \vec{r}_j = -b_{ij} \quad \Longrightarrow \quad \sum \vec{n}_i \vec{r}_j \cdot \vec{r}^i = - \sum b_{ij} \vec{r}^i \quad \stackrel{\text{Eq.(14)}}{\Longrightarrow} \quad n_j = - \sum b_{ij} \vec{r}^i$$

To express the derivatives of the normal vector in terms of the mixed tensor, we need $b_{ij} = \sum g_{jk} b_j^k$ and $\vec{r}^i = \sum g^{ik} \vec{r}_k$:

$$n_j = - \sum b_{ij} \vec{r}^i = - \sum \sum \sum g_{jk} b_i^k g^{ih} r_h \stackrel{\text{Eq.(17)}}{=} - \sum b_i^k \vec{r}_h \delta_j^i \delta_k^h = - \sum b_j^k \vec{r}_k$$

In this way we have derived the Weingarten equations, which express the derivatives of the normal vectors \vec{n} in terms of the dn of the position vectors \vec{r} :

$$\begin{aligned}
\vec{n}_1 &= -b_1^1 \vec{r}_1 - b_1^2 \vec{r}_2 \\
\vec{n}_2 &= -b_2^1 \vec{r}_1 - b_2^2 \vec{r}_2
\end{aligned} \tag{22}$$

We arrived at our first goal, the Weingarten equations. In section 4.4 we will use them to relate a transferred surface element to the curvature and the original surface element. With that we can express the surface given by the interface of the tails and the solvent in terms of the surface given by the cores. But before doing this we will take a look at the principal curvatures of a surface.

4.3 Principal Curvatures

Commonly used parameters for the curvature of a two-dimensional surface are the mean and Gaussian curvature (H and K). In this section we will express them in terms of the coefficients b_j^i defined in the last section, starting from the curvature κ .

Consider a point P on a surface. From point P , there is a normal \vec{n} in the normal direction. Consider a variable plane through the normal. We can evaluate the curvature of the intersecting line. In all directions the curvatures could be different, with exactly one maximum and one minimum. These are the principal curvatures. The directions of the two principal curvatures are orthogonal and are called the principal directions. For some shapes the curvature is in all directions the same, for example on a sphere.

From Eq.(19) and (18), we have:

$$\kappa \stackrel{\text{Eq.(18)}}{=} \underbrace{\sum \sum g_{ij} a^i a^j}_{=1} \stackrel{\text{Eq.(19)}}{=} \sum \sum b_{ij} a^i a^j \Rightarrow \sum \sum \underbrace{(b_{ij} - \kappa g_{ij})}_{c_{ij}} a^i a^j = 0 \quad (23)$$

To find the maximum and the minimum of κ with respect to the direction of the tangent to the curve of interest, we differentiate Eq.(23), regarding κ as a constant (which it is for it extrema). g_{ij} and b_{ij} only depend on the point P , not on the direction. Since we want to find the extrema of κ , depending on the direction and not on the point P where we look at, g_{ij} and b_{ij} remain constant. So we differentiate $\sum \sum c_{ij} a^i a^j = 0$, with c_{ij} constant coefficients.

$$\begin{aligned} \frac{\partial}{\partial a^k} \sum \sum c_{ij} a^i a^j &= \sum \sum c_{ij} \left(\frac{\partial a^i}{\partial a^k} a^j + a^i \frac{\partial a^j}{\partial a^k} \right) \\ &= \sum \sum c_{ij} (\delta_k^i a^j + a^i \delta_k^j) \\ &= \sum c_{kj} a^j + \sum c_{ik} a^i \\ &= \sum (c_{ki} + c_{ik}) a^i \\ &= 2 \sum c_{ik} a^i \end{aligned} \quad (24)$$

When we replace c_{ik} in Eq.(24) for $b_{ik} - \kappa g_{ik}$, and equal it to zero to find the extrema, we obtain:

$$\sum (b_{ik} - \kappa g_{ik}) a^i = 0 \xrightarrow{\text{times } g^{jk}} \sum (b_i^j - \kappa \delta_i^j) a^i = 0 \Rightarrow \sum b_i^j a^i - \kappa a^j = 0 \quad (j = 1, 2)$$

From this equation we can find the principal curvatures. When we write it for $j = 1, 2$ separately, we get:

$$\begin{aligned} (b_1^1 - \kappa) a^1 + b_2^1 a^2 &= 0 \\ b_1^2 a^1 + (b_2^2 - \kappa) a^2 &= 0 \end{aligned}$$

So

$$\begin{pmatrix} b_1^1 - \kappa & b_2^1 \\ b_1^2 & b_2^2 - \kappa \end{pmatrix} \begin{pmatrix} a^1 \\ a^2 \end{pmatrix} = 0 \Rightarrow \begin{vmatrix} b_1^1 - \kappa & b_2^1 \\ b_1^2 & b_2^2 - \kappa \end{vmatrix} = 0$$

$$\Rightarrow (b_1^1 - \kappa)(b_2^2 - \kappa) - b_1^2 b_2^1 = b_1^1 b_2^2 - \kappa(b_2^2 + b_1^1) + \kappa^2 - b_2^1 b_1^2 = \kappa^2 - \sum b_i^i \kappa + \det b_i^j = 0 \quad (25)$$

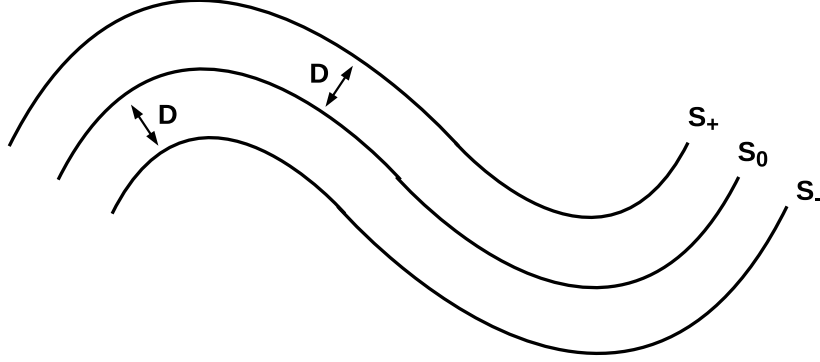


Figure 8: *Transferred surfaces*

To find the extrema of κ (κ_1 and κ_2) we need to solve the quadratic polynomial (25), which leads us to the definition of the mean and Gaussian curvature:

$$\left. \begin{aligned} \kappa_1 &= \sqrt{\frac{1}{4} \left(\sum b_i^i \right)^2 - \det b_i^j + \frac{1}{2} \sum b_i^i} \\ \kappa_2 &= -\sqrt{\frac{1}{4} \left(\sum b_i^i \right)^2 - \det b_i^j + \frac{1}{2} \sum b_i^i} \end{aligned} \right\} \quad \begin{aligned} 2H &= \kappa_1 + \kappa_2 = \sum b_i^i & K &= \kappa_1 \kappa_2 = \det b_i^j \end{aligned} \quad (26)$$

So we have obtained the following two important definitions for the mean curvature H and the Gaussian curvature K :

$$\begin{aligned} 2H &= b_1^1 + b_2^2 \\ K &= b_1^1 b_2^2 - b_2^1 b_1^2 \end{aligned} \quad (27)$$

The Gaussian curvature has an intrinsic sign: it is positive for shapes where κ_1 and κ_2 have the same sign, such as spheres, it is zero for shapes where $\kappa_1 = 0 \vee \kappa_2 = 0$, such as cylinders and it is negative for shapes where κ_1 and κ_2 have an opposite sign, such as saddle points. The sign of the mean curvature depends on definition. Just beneath Eq.(11) we defined the sign of H positive when the normal is on the concave side, so for spheres with the normal pointing outside. And therefore H is negative for spheres with the normal pointing inside.

4.4 Transferred Curved Surfaces

In this section we will finally arrive at the expression we look for: a relation between the surface given by the interface of the tails with the solvent, the principal curvatures and the surface of the cores. To do this we will use the Weingarten equations (Eq.(22)) and the expressions for the mean- and the Gaussian curvature Eq.(27).

When we would transfer a curved surface over a distance D along the normal, depending on the curvature, the surface increases or decreases, as shown in figure 8.

We describe the surface S , with $\vec{r} = \vec{r}(u^1, u^2)$. The distance between the surface S and the

surface S_{\pm} is D along the normal. Hence we can describe the upper and lower surfaces S_+ and S_- , with:

$$S_{\pm} : \quad \vec{r}_{\pm}(u^1, u^2) = \vec{r}(u^1, u^2) \pm D\vec{n}(u^1, u^2) \quad (28)$$

Then, with the definitions of the previous paragraph and the definition of the outer product, a surface element is:

$$d\vec{S} \stackrel{Eq.(12)}{=} \vec{r}_1 du^1 \times \vec{r}_2 du^2 = (\vec{r}_1 \times \vec{r}_2) du^1 du^2 \quad (29)$$

For the surfaces S_+ and S_- we need an expression for \vec{r}_i^{\pm} , like in Eq.(12), but then for the upper and lower surface.

$$\vec{r}^{\pm} \stackrel{Eq.(28)}{=} \vec{r} + D\vec{n} \Rightarrow \vec{r}_i^{\pm} \stackrel{Eq.(13)}{=} \frac{\partial}{\partial u^i} \vec{r}^{\pm} = \frac{\partial}{\partial u^i} \vec{r} + D \frac{\partial}{\partial u^i} \vec{n} = \vec{r}_i + D\vec{n}_i$$

With this, a surface-element at the upper or lower surface is:

$$\begin{aligned} d\vec{S}_{\pm} &= \vec{r}_1^{\pm} du^1 \times \vec{r}_2^{\pm} du^2 = [(\vec{r}_1 + D\vec{n}_1) \times (\vec{r}_2 + D\vec{n}_2)] du^1 du^2 \\ &= [\vec{r}_1 \times \vec{r}_2 \pm D(\vec{r}_1 \times \vec{n}_2 - \vec{r}_2 \times \vec{n}_1) + D^2 \vec{n}_1 \times \vec{n}_2] du^1 du^2 \end{aligned} \quad (30)$$

With the Weingarten equations (22), we can rewrite the outer-product of $\vec{r}_i \times \vec{n}_j$ in terms of only \vec{r}_i and the coefficients b_j^i :

$$\begin{aligned} \vec{r}_1 \times \vec{n}_2 &\stackrel{Eq.(22)}{=} \vec{r}_1 \times [-b_2^1 \vec{r}_1 - b_2^2 \vec{r}_2] = -\vec{r}_1 \times \vec{r}_2 b_2^2 \\ \vec{r}_2 \times \vec{n}_1 &\stackrel{Eq.(22)}{=} \vec{r}_2 \times [-b_1^1 \vec{r}_1 - b_1^2 \vec{r}_2] = -\vec{r}_2 \times \vec{r}_1 b_1^1 = \vec{r}_1 \times \vec{r}_2 b_1^1 \end{aligned} \quad (31)$$

Now we can rewrite Eq.(30), so that the second term becomes:

$$\begin{aligned} D(\vec{r}_1 \times \vec{n}_2 - \vec{r}_2 \times \vec{n}_1) du^1 du^2 &\stackrel{Eq.(31)}{=} -D(b_2^2 + b_1^1)(\vec{r}_1 \times \vec{r}_2) du^1 du^2 \\ &\stackrel{Eq.(29)}{=} -D(b_2^2 + b_1^1) d\vec{S} \stackrel{Eq.(27)}{=} -D(2H) d\vec{S} \end{aligned} \quad (32)$$

And the third term of Eq.(30) becomes:

$$\begin{aligned} D^2 [\vec{n}_1 \times \vec{n}_2] du^1 du^2 &\stackrel{Eq.(22)}{=} D^2 [(-b_1^1 \vec{r}_1 - b_1^2 \vec{r}_2) \times (-b_2^1 \vec{r}_1 - b_2^2 \vec{r}_2)] du^1 du^2 \\ &= D^2 (b_1^1 b_2^2 - b_1^2 b_2^1) (\vec{r}_1 \times \vec{r}_2) du^1 du^2 \\ &\stackrel{Eq.(29)}{=} D^2 (b_1^1 b_2^2 - b_1^2 b_2^1) d\vec{S} \stackrel{Eq.(27)}{=} D^2 K d\vec{S} \end{aligned} \quad (33)$$

Then we obtain for Eq.(30), the following simple expression for the transferred surfaces :

$$d\vec{S}_{\pm} \stackrel{Eqs.(30),(32),(33)}{=} d\vec{S} (1 \mp 2HD + D^2 K) \quad (34)$$

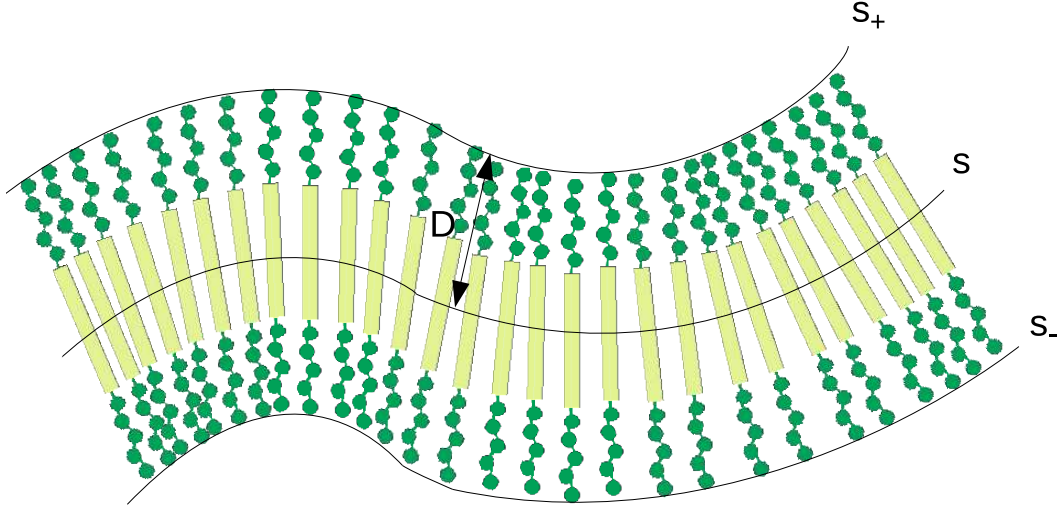


Figure 9: *Curved molecular membrane*

4.4.1 Curved Membranes

For our self-assembled molecular membrane, the surfaces S , S_+ and S_- can be used in the way illustrated in figure 9. S_+ and S_- are the surfaces given by the interface between the tails and the solvent. The surface S is given by the cores. We define the concentration of the cores as n_0 , and the concentration of the tails at S_{\pm} as n_{\pm} . The distance D is the distance along the normal, between S and S_+ as well as between S and S_- . This distance depends on the length of the tails.

Eq.(34) is exactly the equation we were looking for. For a given surface formed by the cores, we can now estimate the surfaces of the interfaces of the tails with the solvent, depending on curvature.

5 Landau Hamiltonian

Lev Landau described, in an ingenious way, a continuous phase transition, from an ordered phase to a disordered phase and vice versa. He assumed that there is an order parameter, which is zero in the disordered phase and non-zero in the ordered phase. The order parameter is small near the critical point (the point where the transition between the ordered and the disordered phase occurs). He stated that one can expand a thermodynamic potential in powers of this order parameter. See for example *Introductory Statistical Mechanics* [5], chapter 12. Lev Landau and Vitali Ginzburg extended the model for order parameters which depend on the spatial coordinates.

In our case we can choose the curvature as an order parameter to describe the transition from a flat to a curved membrane. The radius of the observed vesicles and cylinders (Refs. [10] and [3]) is much larger than the thickness of the membrane, so the curvature is small. This makes curvature an appropriate order parameter. In terms of curvature H and K the Landau-Ginzburg Hamiltonian becomes:

$$F = \int d\vec{S} [AH^2 + c_1H^4 + c_2H^2K + c_3K^2] \quad (35)$$

The odd terms in H , HK and H^3 have to vanish due to the symmetry of the molecules. The other terms respect the symmetry of the molecules. Since the sign of H depends on definition, no linear terms in H are allowed. The sign of K is intrinsic, so K can appear as linear as well as quadratic.

The sign of A determines whether the free energy has a minimum at zero or at a nonzero value of the order parameter, see figure 10. If the minimum is at zero ($A \geq 0$), it means that the

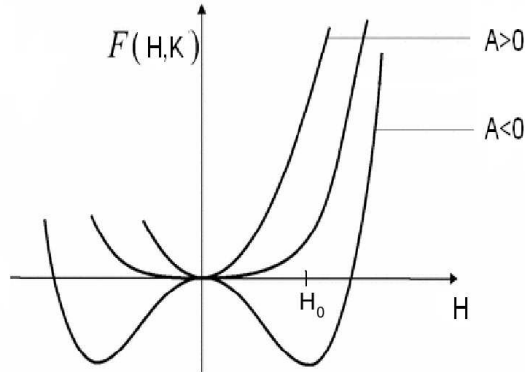


Figure 10: *The free energy, depending on order parameter H*

equilibrium state is a membrane with zero curvature, so a flat membrane. If the minimum is at a certain value H_0 unequal zero ($A < 0$), it means that the equilibrium state is a curved membrane.

In order to have a minimum at all or in other words to have an infinite free energy for infinite curvatures, some of the coefficients should be positive, the free energy as function of curvature should be positive definite. If $A > 0$, there is a minimum at zero and the free energy is infinite for infinite curvatures. If $A < 0$ than $c_1 > 0$ and the determinant of the matrix with the coefficients

c_1 , c_2 and c_3 should be positive, in order to obtain a free energy which is positive definite:

$$c_1 > 0 \quad \text{and} \quad \det \begin{pmatrix} c_1 & \frac{c_2}{2} \\ \frac{c_2}{2} & c_3 \end{pmatrix} > 0 \implies \left| \begin{matrix} c_1 & \frac{c_2}{2} \\ \frac{c_2}{2} & c_3 \end{matrix} \right| > 0$$

$$\implies 4c_1c_3 - c_2^2 > 0 \implies c_2^2 - 4c_1c_3 < 0 \implies c_2 \in (-2\sqrt{c_1c_3}, 2\sqrt{c_1c_3})$$

This means that $c_3 > 0$ so that c_2 is real.

If we analyze the difference in de minima in de Hamiltonian between spheres and cylinders, we can easily see that spheres are preferable above cylinders if $c_2 + c_3 < 0$. And with the same argument cylinders are preferable above spheres if $c_2 + c_3 > 0$. To see this we look for the minima in the Hamiltonian for spheres and cylinders. For a sphere $H = \frac{1}{r}$ and $K = \frac{1}{r_1r_2} = \frac{1}{r^2}$ and for cylinders $H = \frac{1}{r}$ and $K = 0$. This means that for this two shapes the Hamiltonian is:

$$F_{\text{sph}} = \int d\vec{S} [AH^2 + (c_1 + c_2 + c_3)\frac{1}{r^4}] = \int d\vec{S} [AH^2 + (c_1 + c_2 + c_3)H^4]$$

$$F_{\text{cyl}} = \int d\vec{S} [AH^2 + c_1\frac{1}{r^4}] = \int d\vec{S} [AH^2 + c_1H^4] \quad (36)$$

To find the minimum, we take the derivative of the free energy to curvature:

$$\frac{\partial F_{\text{sph}}}{\partial H^2} \int d\vec{S} [A + 2(c_1 + c_2 + c_3)H^2] = 0 \implies H_{\text{minimum sphere}}^2 = \frac{-A}{2(c_1 + c_2 + c_3)}$$

$$\frac{\partial F_{\text{cyl}}}{\partial H^2} = \int d\vec{S} [A + 2c_1H^2] = 0 \implies H_{\text{minimum cylinder}}^2 = \frac{-A}{2c_1} \quad (37)$$

If we substitute the obtained results for H of Eqs.(37) into Eqs.(36), we obtain:

$$F_{\text{min sph}} = \int d\vec{S} \left[-\frac{A^2}{2(c_1 + c_2 + c_3)} + \frac{A^2}{4(c_1 + c_2 + c_3)} \right] = \int d\vec{S} \left[-\frac{A^2}{4(c_1 + c_2 + c_3)} \right]$$

$$F_{\text{min cyl}} = \int d\vec{S} \left[-\frac{A^2}{2c_1} + \frac{A^2}{4c_1} \right] = \int d\vec{S} \left[-\frac{A^2}{4c_1} \right]$$

This means:

$$F_{\text{min sph}} < F_{\text{min cyl}} \quad \text{if} \quad c_1 + c_2 + c_3 < c_1$$

$$\implies c_2 + c_3 < 0 \implies \text{spheres are preferable above cylinders}$$

$$F_{\text{min sph}} > F_{\text{min cyl}} \quad \text{if} \quad c_1 + c_2 + c_3 > c_1$$

$$\implies c_2 + c_3 > 0 \implies \text{cylinders are preferable above spheres} \quad (38)$$

With Eq.(35) we expressed the free energy in terms of curvature. We will jump back to chapter 3 and write the free energy as found in Eq.(9) in the same way as Eq.(35): a free energy density integrated over the surface. That way we can express the coefficients of Eq.(35) in terms of concentration and molecular lengths.

6 Free Energy of Curved Membranes

In this chapter we will first express the concentration of the tails n_{\pm} with help of Eq.(34), in terms of the concentration of the cores n_0 and the principal curvatures. Furthermore we will look at the free energy due to the tail-solvent interactions, by integrating the free energy density over the surface. From this we will obtain an expression of the free energy and we will look at the contribution of the tail-solvent interactions to the coefficients A , c_1 , c_2 and c_3 of the Landau–Ginzburg Hamiltonian of Eq.(35). More precisely we will look at the influence of the length of the tails and solvent molecules. This all following Ref.[6], with the extension of variable length of the solvent molecules.

6.1 Concentration

To express the density of the tails n_{\pm} in terms of the density of the cores, we need the fact, that at S_+ or S_- there are as many tails as there are cores at S :

$$n_{\pm}d\vec{S}_{\pm} = n_0d\vec{S}_0 \implies n_{\pm} = n_0 \frac{d\vec{S}}{d\vec{S}_{\pm}} \stackrel{Eq.(34)}{=} \frac{n_0}{1 \mp 2HD + D^2K} \quad (39)$$

If we now consider the curvatures to be small, we can expand Eq.(39) up until D^4 . This is reasonable in case of the examined molecular membranes, for which the typical order of the radii is Ref.[10] $R \approx 100nm$ while the typical length of the molecules is $l \approx 1nm$. Since $\frac{1}{1+x} \approx 1 - x + x^2 - x^3 + x^4 - \dots$, we obtain:

$$\begin{aligned} n_{\pm} &= n_0 \frac{1}{1 \mp 2HD + D^2K} \\ &\approx n_0 [1 \pm 2HD - KD^2 + 4H^2D^2 \mp 4HKD^3 + K^2D^4 \pm 8H^3D^3 - 12H^2KD^4 + 16H^4D^4] \end{aligned} \quad (40)$$

6.2 Expansion of the Free Energy

In this section we will relate the free energy in terms of concentration and molecular length (Eq.(9)) to the free energy in term of curvature (Eq.(35)). This in order to express the coefficients of the Landau–Ginzburg Hamiltonian (Eq.(35)) in terms of the concentration and the length of the molecules.

Let $\phi(n)$ be the free energy of the mixture of the tails and the solvent per unit volume. So ϕ is a free energy density. We obtain the total free energy by integrating the free energy density over the volume:

$$\delta F = D \int d\vec{S} [\phi(n_+) + \phi(n_-)] \quad (41)$$

This is the free energy of the tail-solvent mixture. This adds up to the terms of the core, which represents the elasticity of the membrane due to the core interactions:

$$F_{\text{core}} = \int d\vec{S} [AH^2 + BK + \dots]$$

To find the expression for $\phi(n_{\pm})$, we will expand $\phi(n)$ around n_0 . Here we assume that the differences in concentrations are small: $n_{\pm} - n_0 \ll 1$. Then, with a Taylor expansion, we obtain:

$$\begin{aligned}\phi(n_{\pm}) \approx & \phi(n_0) + \left. \frac{\partial \phi}{\partial n} \right|_{n=n_0} (n_{\pm} - n_0) + \frac{1}{2!} \left. \frac{\partial^2 \phi}{\partial n^2} \right|_{n=n_0} (n_{\pm} - n_0)^2 \\ & + \frac{1}{3!} \left. \frac{\partial^3 \phi}{\partial n^3} \right|_{n=n_0} (n_{\pm} - n_0)^3 + \frac{1}{4!} \left. \frac{\partial^4 \phi}{\partial n^4} \right|_{n=n_0} (n_{\pm} - n_0)^4\end{aligned}\quad (42)$$

It follows that δF becomes the following equation when we substitute n_{\pm} for the expression as given in Eq.(40). The terms with a \pm sign cancel out because they have opposite sign in $\phi(n_+)$ and $\phi(n_-)$, the other terms are multiplied by a factor 2, because they have the same sign in $\phi(n_+)$ and $\phi(n_-)$:

$$\begin{aligned}\delta F \stackrel{Eq.(41)}{=} & D \int d\vec{S} [\phi(n_+) + \phi(n_-)] \stackrel{Eqs.(42),(40)}{\approx} \\ & 2D \int \left\{ \phi(n_0) + \left. \frac{\partial \phi}{\partial n} \right|_{n=n_0} [-KD^2 + 4H^2D^2 + K^2D^4 - 8H^2KD^4 + 16H^4D^4]n_0 \right. \\ & + \frac{1}{2!} \left. \frac{\partial^2 \phi}{\partial n^2} \right|_{n=n_0} [4H^2D^2 - 24H^2KD^4 + 48H^4D^4 + K^2D^4]n_0^2 \\ & + \frac{1}{3!} \left. \frac{\partial^3 \phi}{\partial n^3} \right|_{n=n_0} [-12H^2KD^4 + 48H^4D^4]n_0^3 \\ & \left. + \frac{1}{4!} \left. \frac{\partial^4 \phi}{\partial n^4} \right|_{n=n_0} [16H^4D^4]n_0^4 \right\} d\vec{S}\end{aligned}\quad (43)$$

From this we can express the coefficients of the tail-solvent free energy that add up to the coefficients of the free energy of the cores. For the different coefficients of equation Eq.(35) we find the following contributions due to the tail-solvent. To find δA , we pick up all terms of Eq.(43) in front of H^2 . For δc_1 are all terms in front of H^4 , for δc_2 are all terms in front of H^2K and for δc_3 all terms in front of K^2 .

$$\delta A = 4D^3 \left[2 \left. \frac{\partial \phi}{\partial n} \right|_{n=n_0} n_0 + \left. \frac{\partial^2 \phi}{\partial n^2} \right|_{n=n_0} n_0^2 \right] \quad (44a)$$

$$\delta c_1 = 4D^5 \left[8 \left. \frac{\partial \phi}{\partial n} \right|_{n=n_0} n_0 + 12 \left. \frac{\partial^2 \phi}{\partial n^2} \right|_{n=n_0} n_0^2 + 4 \left. \frac{\partial^3 \phi}{\partial n^3} \right|_{n=n_0} n_0^3 + \frac{1}{3} \left. \frac{\partial^4 \phi}{\partial n^4} \right|_{n=n_0} n_0^4 \right] \quad (44b)$$

$$\delta c_2 = -4D^5 \left[6 \left. \frac{\partial \phi}{\partial n} \right|_{n=n_0} n_0 + 6 \left. \frac{\partial^2 \phi}{\partial n^2} \right|_{n=n_0} n_0^2 + \left. \frac{\partial^3 \phi}{\partial n^3} \right|_{n=n_0} n_0^3 \right] \quad (44c)$$

$$\delta c_3 = D^5 \left[2 \left. \frac{\partial \phi}{\partial n} \right|_{n=n_0} n_0 + \left. \frac{\partial^2 \phi}{\partial n^2} \right|_{n=n_0} n_0^2 \right] = \frac{\delta A D^2}{4} \quad (44d)$$

We arrived at an expression for the coefficients of the Landau–Ginzburg Hamiltonian (Eq.35) in terms of the free energy and its derivatives as found in chapter 3. In the next section we will investigate them in terms of concentration and molecular length.

6.3 Coefficients of the Landau–Ginzburg Hamiltonian

We found the coefficients in terms of the derivatives of the free energy density. With the Flory–Huggins model in chapter 3, we found the free energy density² in terms of the concentration and the length of the molecules, see Eq.(9). With this equation we can calculate the derivatives of the free energy density per $k_B T$. We now will look specifically at the molecular membranes, with tail molecules denoted by T , with concentration n_T , consisting of r monomers and solvent molecules S , with concentration n_S and consisting of p monomers. We take the derivative with respect to the concentration of the tails.

$$\frac{1}{k_B T} \phi = \chi \frac{pn_S r n_T}{pn_S + rn_T} + n_S \ln \frac{pn_S}{pn_S + rn_T} + n_T \ln \frac{rn_T}{pn_S + rn_T} \quad (45a)$$

$$\frac{1}{k_B T} \frac{\partial \phi}{\partial n_T} = \chi \frac{p^2 n_S^2 r}{(pn_S + rn_T)^2} - \frac{(r-p)n_S}{pn_S + rn_T} + \ln \frac{rn_T}{pn_S + rn_T} \quad (45b)$$

$$\frac{1}{k_B T} \frac{\partial^2 \phi}{\partial n_T^2} = -2\chi \frac{p^2 n_S^2 r^2}{(pn_S + rn_T)^3} + \frac{(r-p)rn_S}{(pn_S + rn_T)^2} + \frac{pn_S}{(pn_S + rn_T)n_T} \quad (45c)$$

$$\frac{1}{k_B T} \frac{\partial^3 \phi}{\partial n_T^3} = 6\chi \frac{p^2 n_S^2 r^3}{(pn_S + rn_T)^4} - \frac{2(r-p)r^2 n_S}{(pn_S + rn_T)^3} - \frac{prn_S}{(pn_S + rn_T)^2 n_T} - \frac{pn_S}{(pn_S + rn_T)n_T^2} \quad (45d)$$

$$\begin{aligned} \frac{1}{k_B T} \frac{\partial^4 \phi}{\partial n_T^4} = & -24\chi \frac{p^2 n_S^2 r^4}{(pn_S + rn_T)^5} + \frac{6n_S r^3 (r-p)}{(pn_S + rn_T)^4} + \frac{2pr^2 n_S}{(pn_S + rn_T)^3 n_T} + \frac{2prn_S}{(pn_S + rn_T)^2 n_T^2} \\ & + \frac{pn_S}{(pn_S + rn_T)n_T^3} \end{aligned} \quad (45e)$$

The distance D depends on the tail length as $D = r\lambda$, with λ the length of one monomer. So combining Eq.(44) and Eq.(45) we find the following dependence of the coefficients in Eq.(44) on concentration and molecular length.

$$\begin{aligned} \frac{\delta A}{k_B T} \stackrel{\text{Eqs. (44a), (45b), (45c)}}{=} & 4(r\lambda)^3 \left\{ 2 \left[\chi \frac{p^2 n_S^2 r}{(pn_S + rn_0)^2} - \frac{(r-p)n_S}{pn_S + rn_0} + \ln \frac{rn_0}{pn_S + rn_0} \right] n_0 + \right. \\ & \left. \left[-2\chi \frac{p^2 n_S^2 r^2}{(pn_S + rn_0)^3} + \frac{(r-p)rn_S}{(pn_S + rn_0)^2} + \frac{pn_S}{(pn_S + rn_0)n_0} \right] n_0^2 \right\} \end{aligned} \quad (46a)$$

²We found the free energy per lattice site, which is the free energy per unit volume, which is the free energy density.

$$\begin{aligned}
\frac{\delta c_1}{k_B T} & \stackrel{\text{Eqs. (44b), (45b), (45c), (45d), (45e)}}{=} 4(r\lambda)^5 \left\{ 8 \left[\chi \frac{p^2 n_S^2 r}{(pn_S + rn_0)^2} - \frac{(r-p)n_S}{pn_S + rn_0} + \ln \frac{rn_0}{pn_S + rn_0} \right] n_0 \right. \\
& + 12 \left[-2\chi \frac{p^2 n_S^2 r^2}{(pn_S + rn_0)^3} + \frac{(r-p)rn_S}{(pn_S + rn_0)^2} + \frac{pn_S}{(pn_S + rn_0)n_0} \right] n_0^2 \\
& + 4 \left[6\chi \frac{p^2 n_S^2 r^3}{(pn_S + rn_0)^4} - \frac{2(r-p)r^2 n_S}{(pn_S + rn_0)^3} - \frac{prn_S}{(pn_S + rn_0)^2 n_0} - \frac{pn_S}{(pn_S + rn_0)n_0^2} \right] n_0^3 \\
& + \frac{1}{3} \left[-24\chi \frac{p^2 n_S^2 r^4}{(pn_S + rn_0)^5} + \frac{6n_S r^3 (r-p)}{(pn_S + rn_0)^4} + \frac{2pr^2 n_S}{(pn_S + rn_0)^3 n_0} + \frac{2prn_S}{(pn_S + rn_0)^2 n_0^2} \right. \\
& \left. \left. + \frac{pn_S}{(pn_S + rn_0)n_0^3} \right] n_0^4 \right\} \quad (46b)
\end{aligned}$$

$$\begin{aligned}
\frac{\delta c_2}{k_B T} & \stackrel{\text{Eqs. (44c), (45b), (45c), (45d)}}{=} -4(r\lambda)^5 \left\{ 6 \left[\chi \frac{p^2 n_S^2 r}{(pn_S + rn_0)^2} - \frac{(r-p)n_S}{pn_S + rn_0} + \ln \frac{rn_0}{pn_S + rn_0} \right] n_0 + \right. \\
& 6 \left[-2\chi \frac{p^2 n_S^2 r^2}{(pn_S + rn_0)^3} + \frac{(r-p)rn_S}{(pn_S + rn_0)^2} + \frac{pn_S}{(pn_S + rn_0)n_0} \right] n_0^2 + \\
& \left. \left[6\chi \frac{p^2 n_S^2 r^3}{(pn_S + rn_0)^4} - \frac{2(r-p)r^2 n_S}{(pn_S + rn_0)^3} - \frac{prn_S}{(pn_S + rn_0)^2 n_0} - \frac{pn_S}{(pn_S + rn_0)n_0^2} \right] n_0^3 \right\} \quad (46c)
\end{aligned}$$

$$\begin{aligned}
\frac{\delta c_3}{k_B T} & \stackrel{\text{Eqs. (44d), (45b), (45c)}}{=} (r\lambda)^5 \left\{ 2 \left[\chi \frac{p^2 n_S^2 r}{(pn_S + rn_0)^2} - \frac{(r-p)n_S}{pn_S + rn_0} + \ln \frac{rn_0}{pn_S + rn_0} \right] n_0 \right. \\
& \left. + \left[-2\chi \frac{p^2 n_S^2 r^2}{(pn_S + rn_0)^3} + \frac{(r-p)rn_S}{(pn_S + rn_0)^2} + \frac{pn_S}{(pn_S + rn_0)n_0} \right] n_0^2 \right\} \quad (46d)
\end{aligned}$$

In the following chapter we will examine the magnitude of this coefficients, due to the solvent-tail interactions and compare them with the magnitude of the coefficient A which represents the elasticity of the membrane mainly due to the core-core interactions.

7 Results

In this chapter we will look at the order of magnitude of the coefficients due to the tail-solvent interactions. For this we assume the following values, determined experimentally in Refs.[3], [10] and [4]:

- Concentration of solvent: $n_S = 6.579 \cdot 10^{27}$ molecules per m^3
- Concentration of tail molecules: $n_T = n_0 = 5.579 \cdot 10^{23}$ molecules per m^3 (This corresponds to $1mg/l$)
- Flory-interaction parameter: $\chi = -1$
- Length of one monomer, or more precisely one unit $\lambda = 1.3 \cdot 10^{-10}m$

The question arises what this concentrations really mean. In this case it is the concentration of the mixture, so before it self-assembled. When the molecules self-assemble, there appear regions with concentrations of 6T higher than given above, but also regions with concentrations lower than that. In the following we will always use the original concentrations. One could question the validity of this approximation.

Another thing one can question is the validity of the choice of $\chi = -1$ as Flory-interaction parameter.

We will look at the coefficients for different values of p , which is the number of units of the solvent molecules and for different values of r , which is the number of units of the tail molecules. We can divide the tail of 6T molecule in units by regarding each CH_2 -group as one unit and each O -atom as $\frac{8}{7}$ unit. This because the diameter of one unit scales with its atomic mass. In Ref.[4] carbon chains are divided in units of 3 CH_2 -groups, with a diameter $d_s = 3,8 \cdot 10^{-10}m$. Then the number of segments n_s is given by the number of CH_2 -groups, C , as: $n_s = \frac{C-1}{3} + 1$. The length D of the molecule is given by:

$$D = (n_s - 1)d_s \quad (47)$$

We will divide the 6T molecule in units of one CH_2 -group. The total length D of the chain is, of course, independent on the way of dividing it in units. So the tail has still length D , divided in $n = C$ segments, with diameter λ , so:

$$D \stackrel{Eq.(47)}{=} (n_s - 1)d_s = \frac{C-1}{3}d_s = \frac{(n-1)}{3}d_s = (n-1)\lambda \quad \implies \quad \lambda = \frac{d_s}{3} \quad (48)$$

From Eq.(48), we see that the length of one monomer, when we divide the tails in monomers consisting of one CH_2 -group, is $\lambda = 1,3 \cdot 10^{-10}m$. When we look at figure 1, we see that one tail consists of approximately 16-17 units.

Next we examine the magnitude and behavior of the free energy and its derivatives. We look at the Eq.(45) in the limit $n_S \gg n_0$. This means that the concentration of the solvent is much bigger than the concentration of the amphiphilic molecules, which is a general situation for self-assemblies. We obtain the following approximations:

$$\frac{\phi}{k_B T} \approx -rn_0 + n_S \ln \frac{pn_S}{pn_S} + n_0 \ln \frac{rn_0}{pn_S} \approx -rn_0 + n_0 \ln \frac{rn_0}{pn_S} \quad (49a)$$

$$\frac{\phi'}{k_B T} n_0 \approx -rn_0 - \frac{r-p}{p}n_0 + n_0 \ln \frac{rn_0}{pn_S} \approx -rn_0 + n_0 \ln \frac{rn_0}{pn_S} + \left(1 - \frac{r}{p}\right)n_0 \quad (49b)$$

$$\frac{\phi''}{k_B T} n_0^2 \approx +\frac{r^2}{p} \frac{n_0^2}{n_S} - \frac{(r-p)r}{p^2} \frac{n_0^2}{n_S} + n_0 \approx +n_0 \quad (49c)$$

$$\frac{\phi'''}{k_B T} n_0^3 \approx -\frac{r^3}{p^2} \frac{n_0^3}{n_S^2} - \frac{(r-p)r^2}{p^3} \frac{n_0^3}{n_S^2} - \frac{r}{p} \frac{n_0^2}{n_S} - n_0 \approx -n_0 \quad (49d)$$

$$\frac{\phi''''}{k_B T} n_0^4 \approx \frac{r^4}{p^3} \frac{n_0^4}{n_S^3} + \frac{(r-p)r^3}{p^4} \frac{n_0^4}{n_S^3} + \frac{r^2}{p^2} \frac{n_0^3}{n_S^2} + \frac{r}{p} \frac{n_0^2}{n_S} + n_0 \approx +n_0 \quad (49e)$$

By examining the magnitude and behavior of these terms, we see from the previous estimations that the free energy and the first derivative of the free energy look rather similar. Since $\frac{n_0^2}{n_S} \ll n_0$ we can neglect the dependence on r and p of the second, third and fourth derivatives.

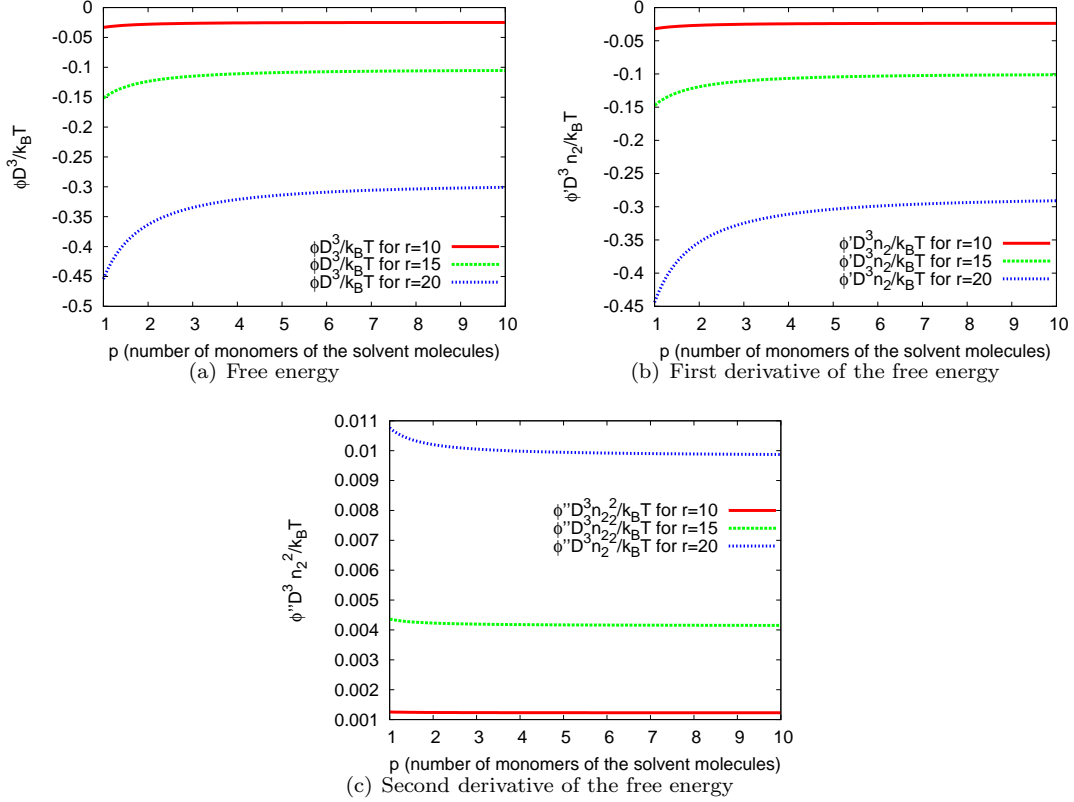


Figure 11: Comparison of the the magnitude of the free energy with its derivatives.

7.1 Results for δA

The term A in the free energy (Eq.(35)) is the crucial term in the free energy, because its sign determines whether the membrane is curved or not. Interesting is the relation between the length of the tails and solvent molecules on one hand and the equilibrium structure (flat or curved) of the membrane on the other hand.

As we see in formula (44a), δA consists of two terms: $D^3 \phi' n_0$ and $D^3 \phi'' n_0^2$. As stated before we

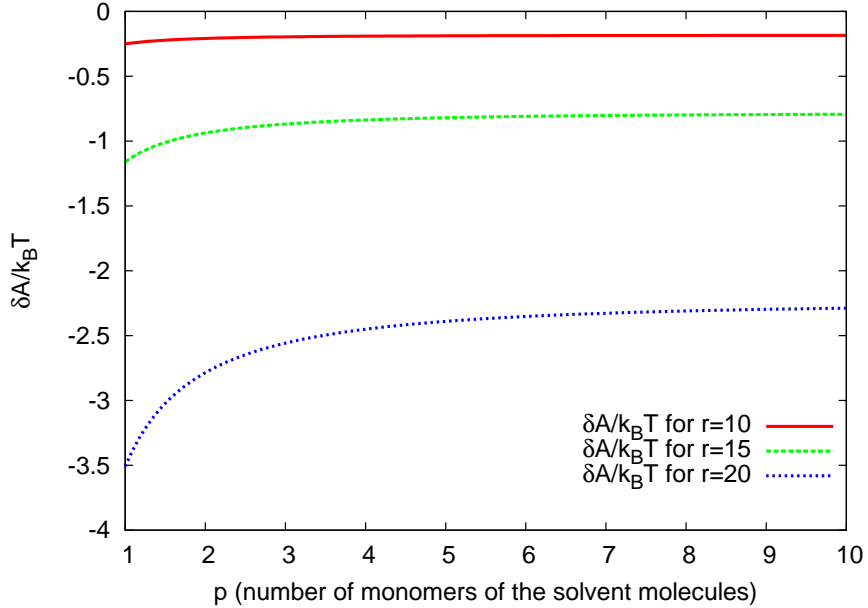


Figure 12: *The coefficient adding up to A in the Landau Ginzburg Hamiltonian.*

can neglect the dependence on r and p of the second derivative. Therefore the only important term, for the dependence on r and p , in δA is the first derivative, which is very similar to the free energy itself. By thinking qualitatively on δA , we could just think of the free energy, which is more intuitive. This you can also see from the figures 11, where the free energy, the first and second derivative are plotted.

When we combine the first and second derivative to δA , we get figure 12. The typical order of magnitude of A (Ref.[9]) as defined in Eq.(35) is $A \approx 10k_B T$. This is the elastic contribution due to the cores. A , the elastic contribution due to the cores, is positive so this coefficient opposes bending, see figure 10. This is in agreement with what we expect for a coefficient which represents the elasticity of the membrane.

We see that the contribution of the tails is of the same order of magnitude, but has the opposite sign. Which means that the contribution of the tail-solvent interactions, could make $A + \delta A$ negative and hence favors bending of the membrane. Experimentally is shown that for certain solvents, vesicles (Ref.[10]) or cylinders Ref.[3] are formed. We find that the length of the solvent molecules does not matter much, but for short solvent molecules the absolute magnitude of δA is slightly bigger. But more important: the longer the tail molecules, the bigger the absolute magnitude of δA . So we expect that for a given length of the tails, only for short solvent molecules, vesicles or cylinders will be formed. And for a given length of solvent molecules, only for long tail molecules vesicles or cylinders will be formed. From the Landau–Ginzburg Hamiltonian we expect that the sign of $A + \delta A$ dictates if the membrane is planar or curved, see figure 10. Since the elasticity coefficient A itself is positive, the sign of $A + \delta A$ depends on the magnitude of δA and probably other contributions. Since δA due to the tail-solvent interactions is negative and of the same order of magnitude as A it could make $A + \delta A$ negative and hence favors bending of the membrane.

7.2 Results for δc_1 , δc_2 and δc_3

The coefficients δc_1 , δc_2 and δc_3 are all in front of fourth-order terms in Eq.(35). Therefore this coefficients give indications about the equilibrium shapes of the membranes. The signs of this coefficients determine certain properties of the equilibrium shape and thus the sign of K . For $c_2 + \delta c_2 + c_3 + \delta c_3 > 0$ cylinders are preferable above spheres, whereas spheres are preferable above cylinders for $c_2 + \delta c_2 + c_3 + \delta c_3 < 0$, see Eq.(38).

From Eq.(44) and the estimations of Eq.(49), we can now make an estimation of the coefficients δc_1 , δc_2 and δc_3 , compared with δA (The estimations are done for tail molecules consisting of 5 till 20 units (and less important for solvent molecules from 1 till 10 units)). Since the first derivative is the dominant term for the dependence on r and p , the dependence on r and p of the coefficients δc_1 , δc_2 and δc_3 is the same as of δA . Only the magnitude and the sign vary.

$$\frac{\delta A}{k_B T} \approx (r\lambda)^3 \{8\phi' n_0 + 4n_0\} \approx -10^{-2} \text{ till } -1 < 0 \quad (50a)$$

$$\frac{\delta c_1}{k_B T} \approx (r\lambda)^5 \{32\phi' n_0 + 44\frac{1}{3}n_0\} \approx (-10^{-20} \text{ till } -10^{-17})m^2 < 0 \quad (50b)$$

$$\frac{\delta c_2}{k_B T} \approx (r\lambda)^5 \{-24\phi' n_0 + 5n_0\} \approx (10^{-20} \text{ till } 10^{-17})m^2 > 0 \quad (50c)$$

$$\frac{\delta c_3}{k_B T} \approx (r\lambda)^5 \{2\phi' n_0 + n_0\} \approx (-10^{-21} \text{ till } -10^{-18})m^2 < 0 \quad (50d)$$

Again only the first derivative of the free energy is important and we see that the length of the solvent molecules is not very important. The length of the tails does matter. We see that the longer the tails, the bigger the absolute value of the coefficients.

In Ref. [7] the best fit to the experiment gave the following values of the coefficients:

$$\begin{aligned} \frac{c_{1\text{tot}}}{k_B T} &\approx 2.77 \cdot 10^{-16} m^2 \\ \frac{c_{2\text{tot}}}{k_B T} &\approx -3.22 \cdot 10^{-16} m^2 \\ \frac{c_{3\text{tot}}}{k_B T} &\approx 0.86 \cdot 10^{-16} m^2 \end{aligned} \quad (51)$$

The subscript *tot* denotes that the total coefficient is meant, including all kind of contributions. These values are for 6T molecules in isopropanol. Comparing this results to the estimated contribution of the tail-solvent interactions, given in Eq.(50), we find that the calculated magnitudes, for $r = 20$ are still one order of magnitude smaller than found in 51.

If we look at the Landau–Ginzburg Hamiltonian, Eq.(35), we first find that a curved surface is preferable when $A + \delta A < 0$, and moreover we could find that cylinders are preferable when $c_2 + \delta c_2 + c_3 + \delta c_3 > 0$ and spheres are preferable when $c_2 + \delta c_2 + c_3 + \delta c_3 < 0$ (see Eq.(38)). However, there is a problem. The tail-solvent interactions destabilize not only the bending (harmonic) contribution ($\delta A < 0$) as was shown in Ref. [6] but also the fourth-order (anharmonic) contribution to the extended free energy written in terms of the curvature. To stabilize the free energy we must conclude that the solvent-tail interaction, which we calculated, are not the only important interactions and therefore not the only important contribution to the free energy. Some of the coefficients c_1 , c_2 , c_3 due to other interactions than the solvent-tail interactions, should be unequal zero.

8 Conclusion

In this report I looked at the solvent-tail interactions in molecular self-assembled membranes. I investigated their contribution to the free energy, by looking at their contributions to the coefficients of the Landau-Ginzburg Hamiltonian (Eq.(35)).

For the coefficient A of the term H^2 , the coefficient due to the tail-solvent interactions has the same order of magnitude as the coefficient due to the cores, which represents the bending rigidity of the membrane. The coefficient due to the cores is positive, which means that the membrane opposes bending, while the coefficient due to the solvent-tail interactions is negative. This means that this contribution could make the total coefficient negative, which implies that a curved state is favorable.

From figures 11 and 12, we saw that the length of the solvent-molecules is not very important for the magnitude of the coefficients. The length of the tail-molecules is dominant. For longer tails, the absolute value of the coefficient due to the contribution of the tail-solvent interactions is the biggest.

The contributions to c_1 , c_2 and c_3 in Eq.(35) destabilize the minimum of the free energy, which implies that the tail-solvent interactions are not the only important interactions. Moreover, when we compare the magnitudes with experimentally found values, the calculated coefficients are rather small compared to the values extracted by fitting to the experiment. This could as well mean that there are also other contributions.

9 Perspectives

It would be interesting to verify the obtained theoretical expectations, with systematic experimental investigations on the role of the length of the tails and the solvent.

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