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Topological defects in lamellar phases: passages, and their fluctuations

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Abstract. — In lamellar phases of ternary amphiphilic mixtures, passages are tube-like connections of neighboring oil- (or water-) layers. Passages form spontaneously due to the thermal fluctuations of the monolayers (or membranes), which separate oil and water. Analogous membrane conformations also exist in binary amphiphilic mixtures, where the membranes are amphiphilic bilayers. We study the shape and the fluctuations of passages. Our analysis is based on the curvature model of fluid membranes, both with and without spontaneous curvature. Passages have a very small bending energy, and show strong fluctuations. The mean radius, the fluctuations of the radius, and the asphericity of the passage are calculated. All these quantities are experimentally accessible.

1. Introduction.

Many complex phases are formed when amphiphilic molecules are added to mixtures of oil and water [1, 2]. It depends on temperature as well as the concentrations of all components, which of these phases is thermodynamically stable. One of the most prominent and well studied phases is the lamellar phase. It occurs in a binary system of water and amphiphile, where the amphiphiles form bilayers which are separated by layers of water. In some cases, the separation of the bilayers has been found to be as large as several thousand Å [3-5]. Lamellar phases also occur, of course, in ternary systems, where they consist of alternating layers of oil and water, which are separated by amphiphilic monolayers.

Two mechanisms are responsible for the enormous separations between mono- or bilayers, which we will collectively call membranes. The first is the long-range electrostatic interaction between equally charged surfaces, the second is an entropic interaction, which is due to the thermal fluctuations of the membranes [6]. As long as electrostatic interactions are present, they dominate at large distances, and suppress membrane fluctuations [7]. However, by adding a sufficiently large amount of salt to the system, the electrostatic interaction can be screened and becomes effectively short ranged. We will assume that this is the case in the systems studied here.
Since membranes are (nearly) tensionless surfaces, their shapes and fluctuations are controlled by the elastic curvature Hamiltonian [8]

$$\mathcal{H}_{\text{curv}} = \int dS \left[ 2\kappa (H - H_0)^2 + \tilde{\kappa} K \right]$$

(1)

where $H = (1/R_1 + 1/R_2)/2$ is the mean curvature and $K = 1/R_1 R_2$ the Gaussian curvature, both given in terms of the principle radii of curvature, $R_1$ and $R_2$. $H_0$ is the spontaneous curvature, which tends to bias the mean curvature of the membrane. The integral in (1) is over the whole membrane. The bending rigidity $\kappa$ and the saddle-splay modulus $\tilde{\kappa}$ determine the elastic bending energy of the membrane.

It is the restriction of the membrane fluctuations in the stack due to the neighboring membranes which reduces the entropy of the fluctuations. Each time a membrane collides with its neighbors, it loses entropy of order $k_B$ compared to a free membrane [9]. The entropy loss per unit area is thus $k_B/\xi_{\|}^2$, where $\xi_{\|} \sim \sqrt{\kappa/k_B} T d$ is the parallel correlation length [10-12], and $d$ is the average membrane separation. This leads to the effective repulsive interaction of the form $V_{\text{eff}} \sim \kappa^{-1}(k_B T)^2 d^{-2}$ [6]. It has been confirmed experimentally that there is indeed such an effective interaction between neighboring membranes [3, 7, 13].

Since each membrane in the stack must collide with its neighbors quite frequently due to thermal fluctuations, it has been speculated [14, 15] that some of these collisions lead to the formation of channels, or passages, perpendicular to the membranes. In a ternary system, the passages are formed between neighboring oil- (or water-) layers, thus connecting neighboring monolayers. Similarly, in binary systems they form a connection between neighboring bilayers. Passages have been observed experimentally in oil-water-surfactant mixtures, both in systems with ionic [16] and non-ionic [17] amphiphiles. Passages have also been found in Monte Carlo simulations [18, 19] of binary and ternary amphiphilic mixtures. Finally, passages have been seen in multi-lamellar vesicles of a binary lipid-water system [20]. We will often call the channels "wormholes", a name which is used for a similar geometry in gravitation theory.

We want emphasize that we consider here only the case of a symmetric lamellar phase, where the average thickness of the oil- and water-layers in a ternary system is identical. In the limit of a very small oil- or water-concentration, the passages become holes in a single bilayer [21-23]. Since the curvature at the edge of a bilayer is very large, the elastic curvature Hamiltonian (1) is not sufficient to calculate the size of the holes in this limit.

The first attempt to calculate the shape of wormholes with the use of the curvature model (1) is due to Harbich et al. [20]. They found that there are solutions of the Euler-Lagrange equations which have roughly the expected shape. In fact, their solution is a minimal surface, the catenoid. However, it can be easily seen that the catenoid cannot be a true wormhole, because it does not satisfy the boundary conditions for two membranes connected by a wormhole, which are embedded in a stack of other membranes. At large radial distances the membranes must be flat and parallel to each other, which is not the case for the catenoid.

In this paper we want to discuss the shape of a single wormhole. Our calculation is based on the Hamiltonian (1). Since the membrane fluctuations stabilize the lamellar phase, a calculation of the shape of a wormhole has to include the effect of fluctuations. To make the problem tractable, we study the fluctuations of two membranes which are connected by the wormhole, but replace the interaction of all membranes by an effective potential $V_{\text{eff}}$, which is derived from the steric repulsion discussed above. Thus, we have the partition function

$$\mathcal{Z} = \int \mathcal{D}\mathbf{X} \exp \left[ -\beta \left( \mathcal{H}_{\text{curv}}\{\mathbf{X}\} + \int dS V_{\text{eff}}\{\mathbf{X}\} \right) \right]$$

(2)
where $H_{\text{curv}}$ is the Hamiltonian (1) and $\beta = 1/k_B T$. The integration in (2) extends over all conformations of the membrane with the topology of a wormhole consistent with the appropriate boundary conditions. There are no further constraints, in particular the area of the membrane is not fixed.

The paper is organized as follows. In section 2 we employ mean-field theory, i.e. we minimize the Hamiltonian (1) together with the effective potential describing the steric interaction. As shown above, the strength of this potential is temperature dependent. Therefore, the mean-field results depend on temperature. Due to the scale invariance of (1), the size of the hole is determined only by the boundary conditions, i.e. by the distance of the two membranes far away from the wormhole. This leads to wild fluctuations of the shape of the passage. Therefore, we study in section 3 the influence of fluctuations on the size and shape of a wormhole. In section 4 we discuss the stability of wormholes with non-zero spontaneous curvature. A summary concludes the paper in section 5.

2. Mean field theory.

To calculate the shape of a wormhole, we first consider a finite system, and then take the limit of large system size. The geometry we consider is shown in figure 1.

The boundaries of the two membranes, which are connected by the wormhole, are two circular rings of radius $r_1$ a distance $d$ from one another. For sufficiently large $r_1$, the membranes should become nearly flat at large radial distances and the shape of the wormhole should become independent of $r_1$. Assuming rotational symmetry, we can parametrize the membrane by a surface of revolution of the curve $C = (r(s), z(s))$, where $s$ is the arc-length of $C$ measured from $z = 0$ [24, 25]. By introducing the angle $\psi$ between the $x$-axis and the tangent of $C$, the mean curvature $H$, the Gaussian curvature $K$ and the area element $dS$ in (1) can be written as $2H = \psi' + \sin \psi/r$, $K = \psi' \sin \psi/r$, and $dS = 2\pi r ds$, where the prime denotes $d/ds$. Assuming symmetry with respect to reflections at $z = 0$, we can restrict ourselves to $z > 0$, with the boundary conditions

$$\begin{align*}
\psi(0) &= \pi/2 & r(s_1) &= r_1 \\
\psi''(0) &= 0 & \psi(s_1) &= 0 \\
z(0) &= 0 & z(s_1) &= d/2
\end{align*}$$

(3)

**Fig. 1.** — a) Schematic geometry of a wormhole; b) parametrization of the membrane.
Because the area of the membrane is not fixed, we also have to minimize the curvature Hamiltonian with respect to \( s_1 \). The contribution of the Gaussian curvature to \( \mathcal{H} \) can be shown to be a constant; this reflects the fixed topology of the wormhole geometry. Therefore, \( \kappa \) is set equal to zero in the following.

Let us first ignore the entropic interaction between the membranes. In this case, the shape of the wormhole is obtained by minimizing the functional

\[
\mathcal{L} = \pi \int_0^{r_1} ds \left[ \kappa r \left( \psi' + \sin \psi - 2H_0 \right)^2 + \gamma (r' - \cos \psi) + \eta (z' - \sin \psi) \right]
\]

with the boundary conditions (3), and Lagrangian multipliers \( \gamma(s) \) and \( \eta(s) \). In the limit \( r_1 \to \infty \) and with vanishing spontaneous curvature, the shape of a wormhole is found to become singular; both the inner radius \( r_0 = r(0) \) and the mean distance between the two membranes tend to zero in this limit. Indeed, for \( r_0 \to 0 \) the solution is almost a catenoid, \( r(z) = r_0 \cosh(z/r_0) \), which is the minimal surface calculated by Harbich et al. [20]. Because \( z(r) \) grows very slowly with increasing \( r \), the distance between the upper and the lower membrane is very small. Therefore the interaction of the two membranes becomes important and must be taken into account, if one wants to calculate the shape of a wormhole. Because the interaction is repulsive, it favors larger passagges, and therefore competes with the curvature energy, which favors infinitesimal small wormholes. Thus, the steric interaction leads to a finite inner radius of the wormhole, even in the limit \( r_1 \to \infty \).

To include the steric interaction we introduce an effective potential \( V_{\text{eff}} \), as mentioned in the introduction. The form of \( V_{\text{eff}} \) is restricted by the following conditions: i) it should act on the projection of the membranes onto a \( z = \)const plane; therefore, \( V_{\text{eff}} \) has to be \( \pi \)-periodic in \( \psi \); ii) the fluctuations of a planar membrane at \( z = \pm d/2 \) should be restricted by the potential in such a way that \( (z - (z))^2 = \mu d^2 \), with \( \mu \) of order unity [6]. This leads to an effective interaction potential with a \( d^{-2} \)-decay. It has been argued in reference [6] that \( \mu = 1/6 \) should be used. This value is in reasonable agreement with the value \( \mu = 0.130 \) obtained from Monte Carlo simulations for a single membrane between two hard walls [26], and will be used for all numerical calculations presented below. For calculational reasons \( V_{\text{eff}} \) should also be continuous and differentiable in \( z \) and \( \psi \). The simplest way to fulfill these conditions is to choose \( V_{\text{eff}} \propto 1/4 \) proportional to \( \cos^2(\pi z/d) \cos^2 \psi \). For reasons that will discussed below we found that such a potential is not a good approximation if \( |z| \) becomes greater \( d/2 \). Therefore, we chose instead

\[
V_{\text{eff}}(z, \psi) = \frac{\kappa d^4}{8 \xi^4} \left( (z/d)^2 - 1/4 \right)^2 \cos^2 \psi
\]

where \( \xi \) is determined by the condition (ii) above, which leads to the implicit equation

\[
\mu d^2 = \frac{k_B T}{8 \kappa} \left( \frac{1}{4 \xi^4} - H_0^2 \right)^{-1/2} \left[ 1 - \frac{2}{\pi} \arctan \frac{2H_0^2 \xi^2}{(1 - 4H_0^2 \xi^4)^{1/2}} \right].
\]

For \( H_0 = 0 \), this simplifies to \( \xi = 2d \sqrt{\mu k_B T} \). Typical values for the parallel correlation length are \( \xi/d = 2.8 \) for \( \kappa/k_B T = 3 \), \( H_0 = 0 \), and \( \xi/d = 2.0 \) for \( \kappa/k_B T = 3 \), \( H_0 d = 0.1 \). Note that \( V_{\text{eff}} \) only depends on \( z/d \); therefore, if \( H_0 \) is measured in units of \( 1/d \), the membrane separation \( d \) enters the model only as a scale parameter. \( V_{\text{eff}} \) is in some way arbitrary, of course, but we believe that other choices should not change our results qualitatively.

The minimization of (4), (5) with the boundary conditions (3) leads to the Euler-Lagrange equations

\[
r' = \cos \psi
\]
Fig. 2. — Solutions of the Euler-Lagrange equations with $\beta\kappa = 1.19$ and $r_1 = 7.5\ d$. The full line is the mean-field solution, with radius $r_0 = 0.3$. The dashed line is calculated with fixed $r_0 = 1.0$.

\[
\begin{align*}
z' &= \sin \psi \\
\gamma' &= \psi'^2 - \frac{\sin^2 \psi}{r^2} + H_0^2 - 2H_0 \psi' + \frac{2}{\kappa} V_{\text{eff}}(z, \psi) \\
\eta' &= \frac{d^2}{\xi_{\parallel}^4} \cos^2 \psi \ z((z/d)^2 - 1/4) \\
\phi'' &= \frac{-\psi' \cos \psi + \sin \psi \cos \phi}{r} + \frac{\gamma \sin \psi - \eta \cos \psi}{2r} \\
&\quad + H_0 \frac{\cos \psi}{r} + \frac{d^4}{4\xi_{\parallel}^4} \cos \psi \sin \psi ((z/d)^2 - 1/4)^2
\end{align*}
\]

A first integral of equations (7) is given by

\[
I = -r(\psi')^2 + \frac{\sin^2 \psi}{r} + 4H_0^2 r - \frac{2}{\kappa} r V_{\text{eff}}(z, \psi) - \gamma \cos \psi - \eta \sin \psi.
\]

Minimization with respect to the free upper boundary $s_1$ implies $I = 0$ [25], which gives the additional boundary condition $-(\psi'(s_1))^2 r(s_1) = \gamma(s_1)$. Solution of the equations (7) has been obtained numerically with the use of a shooting method. In this section we only want to consider membranes without spontaneous curvature, i.e. $H_0 = 0$, as is the case for amphiphilic bilayers. A typical conformation of a wormhole in this case is shown in figure 2. Because $\xi_{\parallel}$ depends on $\beta$, the shape changes with temperature. However, the mean-field radius $r_0$ depends only very weakly on temperature, as shown in figure 3. It decreases from $r_0 = 0.15\ d$ at $\beta\kappa = 1$ to $r_0 = 0.12\ d$ at $\beta\kappa = 5$. The decrease is due to a smaller steric interaction at lower temperatures; as discussed above, $r_0$ vanishes if the steric interaction is neglected. Thus, the steric interaction increases the radius $r_0$. The free energy of the wormholes is dominated by the steric interaction. Therefore, it is of the order of $\kappa d^4/\xi_{\parallel}^4$, which can be as small as $10^{-2}\kappa$ for $\beta\kappa = 5$.

To check the assumption that the boundary conditions do not influence the shape of the passage, we linearize the Euler-Lagrange equations (7) for large $s$. This leads to

\[
s^2 \eta^{(4)} + s\eta^{(3)} - \eta'' + \frac{d}{2\xi_{\parallel}^4} s \eta = 0
\]
Fig. 3. — Radius $<r_0>$ of a passage, as a function of $\kappa/k_B T$, both in the mean-field approximation (dashed line) and with fluctuations (solid line).

and

$$\eta'' = \frac{d}{\xi_{||}^4} \psi.$$  \hfill (10)

If $\xi_{||} = \infty$, i.e. if there is no steric interaction, the passage is a catenoid, and the curvature decays as $s^{-2}$. But if $\xi_{||} < \infty$, the solutions of (9) show asymptotically an exponential decay. Therefore, $\psi$ and the mean curvature also vanish exponentially. Together with our numerical results for different $r_1$, this shows clearly that a sufficiently large but finite radius $r_1$ does not affect the shape of the passage. This result also implies that the lateral interaction between two wormholes decays exponentially.

It is also interesting to determine the shape of a passage with fixed inner radius $r_0$. We do this by introducing a term $\delta(s)(r(0) - a)^2$ in the free energy density, where $\delta(s)$ is the Dirac $\delta$ function. This is equivalent to introducing an additional constraint $r(0) = r_0(a)$, with an associated Lagrangian multiplier, or to solving the above differential equations with the boundary condition $r(0) = r_0$ instead of $\psi''(0) = 0$. For large $r_0$, the free energy of this conformation can be understood as the line tension of a linear edge of a folded membrane, confined in a stack of other membranes. In this case, one of the principal curvatures becomes very small, and can therefore be neglected. Then the curvature Hamiltonian reduces to

$$H_{\text{curv}} \approx \pi \kappa \int_0^{x_1} ds \, r(\psi)'^2 \approx 2\pi \kappa r_0 \int_0^{x_1} ds \, (\psi')^2.$$  \hfill (11)

The minimization of this Hamiltonian with the boundary conditions (3) can be done exactly. The result for the free energy is

$$F(r_0) = \pi \kappa \left[B\left(\frac{3}{4}, \frac{3}{4}\right)\right]^2 \frac{r_0}{d}.$$  \hfill (12)

where $B$ is the Beta function, with $B(3/4, 3/4) \approx 1.2$.

The conformation shown in figure 2 exhibits a hump just outside the passage, which grows with increasing $r_0$ and $\xi_{||}$, i.e. increasing $\beta \kappa$. If we use a $z$-periodic potential as discussed above, this hump would “jump” over the maximum of the potential at $z = d$. This would correspond to an interpenetration of two membranes, and is clearly unphysical. The same problem does not occur with the potential (5). Nevertheless, if the hump gets too large, the potential $V_{\text{eff}}$ is no longer a good approximation to describe the effect of self-avoidance.
3. Fluctuations of the wormhole.

In the last section, we have calculated the free energy as a function of the hole-radius $r_0$. This result can be used to estimate the fluctuations of the size of the wormhole. We find $\Delta r_0/r_0 \approx 0.6$ for $\kappa$ of order $k_B T$, with a very weak temperature dependence. Thus, the size and the shape of a wormhole must be strongly influenced by fluctuations.

To calculate the contribution of fluctuations to the partition function $Z$, the simplest approximation is to expand $\mathcal{H}$ around the mean-field solution to second order in $k_B T/\kappa$. This Gaussian (or capillary wave) approximation is valid if the amplitudes of the fluctuations are small. However, $\Delta r_0$ calculated within this approximation is about as large as the above estimate, so that the condition $\Delta r_0 \ll r_0$ is not fulfilled. The breakdown of the Gaussian approximation is due to a soft mode with an eigenvalue of the order of $\kappa d^4 \xi^{-4}$. This soft mode changes the size of the wormhole, while keeping its shape roughly fixed; we will therefore call it the "breathing mode". The low energy of the breathing mode is quite understandable, considering that the inner part of the passage is approximately a (scale invariant) minimal surface. We solve the problem of this soft mode by treating fluctuations in $r_0$ exactly. To do so, we insert a 1 in the partition function (2), and then interchange the order of integration,

$$Z = \int_{-\infty}^{+\infty} da \sqrt{\alpha/\pi} \int D\mathbf{x} e^{-\alpha(f_0 - a)^2} \exp(-\beta\mathcal{H}(\mathbf{X}))$$

$$= \sqrt{\alpha/\pi} \int_{-\infty}^{+\infty} da \ e^{-\beta F(a)}$$

(13)

with $r_0 = \int_0^{2\pi} r(s = 0, \phi) d\phi/2\pi$, where $\alpha$ is chosen such that the fluctuations of $r_0$ with fixed $a$ are much smaller than $r_0$. In our calculations, we use $\alpha = 200\beta kd^{-2}$. The mean-field value of $F(a)$ is obtained by calculating the passages with fixed $r_0$ as indicated at the end of the last section. The contribution of the quadratic potential in (13) to the Euler-Lagrange equations leads to a discontinuity in the second derivative of the profile at $z = 0$, because the potential acts only in the $z = 0$ plane. Since the integration over $a$ extends to $-\infty$, negative values of $r_0$ are possible. Such unphysical solutions are avoided by introducing a hard wall at $r_0 = 0$. Since the free energy of these solutions is very high compared to the mean-field solution, their contribution to the partition function is negligible.

In order to sum only over physically inequivalent configurations, we have to select a unique parametrization for the fluctuating membrane. Here physically inequivalent means that two configurations cannot be transformed into each other by a reparametrization. This is done in the following way. All configurations not too far from the mean-field configuration $\mathbf{X}_a = (r(s) \cos \phi, r(s) \sin \phi, z(s))$ (for a given parameter $a$) can be written as

$$\mathbf{X}(s, \phi) = \mathbf{X}_a(s, \phi) + \nu(s, \phi) \mathbf{n}_a(s, \phi)$$

(14)

where $\mathbf{n}_a(s, \phi)$ is the normal vector of the mean-field surface. The integral over $D\mathbf{X}$ is now an integral over all $\nu(s)$, multiplied by the Faddeev-Popov determinant [27, 28]

$$\det J = \prod_S \det [g^0_{ij}(S) + \partial_i(\nu(S)\mathbf{n}(S))\partial_j\mathbf{X}_a(S)] \ / \det g^0_{ij}(S)$$

(15)

with $i, j \in \{s, \phi\}$, $g^0_{ij}$ is the metric on $\mathbf{X}_a$ and $\prod_S$ is a (formal) product over all points on the membrane. The Faddeev-Popov determinant makes sure that only those fluctuations are taken into account in the functional integral, which are orthogonal to reparametrizations. Then the
partition function for fixed $a$ reads
\[
\exp(-\beta F(a)) = \int \prod_S d\nu(S) \exp \left[ -\beta H_{\text{curv}} - \int dS (\beta V_{\text{eff}} - \log \det J) \right].
\]

The expansion to second order in the fluctuations $\nu$ leads to
\[
\log \det J = 2H\nu + K\nu^2
\]
and
\[
g_{ij} = g_{ij}^0 - 2\nu C_{ij} + \nabla_i \nabla_j \nu + \nu^2 C_{ij} C_{ij}.
\]
where $H$, $K$ are the mean and Gaussian curvature of the mean-field conformation, and $g_{ij}$ and $C_{ij}$ are the first and the second fundamental forms in this geometry, respectively. $\nabla$ denotes the covariant derivative. The result for the expansion of the curvature energy $H^2$ and potential $V_{\text{eff}}$ are given in the Appendices A and B. The linear terms in the expansion of $H^2$ and $(\det g)^{1/2}$ vanish identically because we expand around a minimum of the free energy. Putting everything together, we arrive at
\[
-\beta F(a) = -\beta F_{\text{mf}}(a) \quad \text{(19)}
\]
\[
- \int \prod_S d\nu(S) \exp \left[ -\int r ds d\phi (\nu L(s) + \nu O(s, \phi)) \right]
\]
where $F_{\text{mf}}$ is the free energy of the mean-field solution $r(s)$, $L = 2H$ is due to the linear term in the expansion of the Faddeev-Popov determinant (17), and $O(s, \phi)$ is a hermitian operator, which is obtained by collecting all the quadratic terms in $\nu$. For the flat part of the membrane, $O$ reduces to $\frac{1}{2} \beta \kappa \left[ (\nabla^2)^2 + \xi^4 \right]$.

To integrate over $\nu(S)$, we have to define the measure $\prod_s d\nu(S)$. This is done in the usual way [29] by expanding $\nu$ in a set of eigenfunctions of the operator $O$, $\nu = \sum_n \alpha_n \nu_n$, and writing $\prod_s d\nu(S) = \prod_n d\alpha_n$. A further simplification arises from the rotational symmetry of our problem, which allows an expansion in terms of eigenfunctions of angular momentum,
\[
\nu(s, \phi) = \sum_m \sum_i \nu_i^m(s) (\alpha_i^m \sin m\phi + \beta_i^m \cos m\phi).
\]

The eigenfunctions $\nu_i^m$ are either even or odd functions of $s$, due to the reflection symmetry with respect to the $z = 0$ plane of the operator $O$. The boundary conditions for odd eigenfunctions are $\nu(s_1) = \nu'(s_1) = 0$ and $\nu(0) = \nu''(0) = 0$, and for the even eigenfunctions $\nu'(0) = 0$ and $\nu''(0) = (\psi''(0) (1/r_0 - 3\psi'(0)) - \alpha/r_0) \psi(0)$. The non-vanishing third derivative in the latter case is due to the discontinuity of the third derivative of the mean-field profile. On the flat part of the membrane, $\nu_i^m$ are solutions of Bessel's differential equation, with wavevector $k_i^m$ and eigenvalue $E_i^m = \kappa (k_i^m)^4 + \xi_{\parallel}^{-4}/2$. The curvature dependent terms in $O$ can be neglected if $1/k_i^m \ll r_0$. In this limit one obtains a spectrum with spacing $\Delta k = \pi/s_1$.

After inserting the expansion (20) in (19) and doing the Gaussian integrals we arrive at
\[
\beta F(a) = \beta F_{\text{mf}}(a) \quad \text{(21)}
\]
\[
- \sum_{m=0}^{\infty} (2 - \delta_{m0}) \sum_i \left[ \frac{1}{2} \log \frac{\pi}{\beta E_i^m} + \frac{(L_i^m)^2}{4\beta E_i^m} \right]
\]
where $E_i^m$ are the eigenvalues belonging to $\nu_i^m$ and $L_i^m = 4\pi \delta_m \int_0^{r_i} ds L(s) \nu_i^m(s)$. The sums in equation (21) have a divergence at high energies. We therefore regularize them by using an exponential decreasing cutoff function, $\sum_{m,i} f(E_i^m) \to \sum_{m,i} \exp(-E_i^m/E_c) f(E_i^m)$. It is important to use a soft cutoff, because the membrane is finite and hence the eigenvalues are discrete. Otherwise the free energy would vary discontinuously with the number of eigenvalues with $E_i^m \leq E_c$.

The free energy $F(a)$ has not only contributions from the wormhole, but also from the flat part of the membrane. In fact, the free energy of a large membrane is dominated by the free energy of the flat part. Therefore, in order to extract the contribution of the wormhole, we subtract the free energy of a flat circular membrane with the same area, calculated with the same cutoff. The eigenfunctions of a flat circular membrane are given by a linear combination of Bessel functions, $\nu_i^m(s) = \alpha_i^m J_m(k_i^ms) + \beta_i^m J_m(k_i^ms) \delta$, where $\alpha_i^m$, $\beta_i^m$ and $k_i^m$ are determined by the boundary conditions $\nu_i^m(s_1) = \nu_i^m(s_1)/ds_1 = 0$, and the normalization.

From (13) we can calculate the mean size of the wormhole

$$\langle r_0 \rangle = \int \frac{\text{d}a \bar{r}_0 \exp(-\beta F(a))}{\int \text{d}a \exp(-\beta F(a))},$$

where

$$\bar{r}_0 = \int_0^{2\pi} \frac{d\phi}{2\pi} r(s=0, \phi)$$

is the mean inner radius of a configuration. The eigenvalue equation is solved numerically with a finite difference method for $\beta \kappa = 1.19$, $3.0$ and $5.0$, with zero spontaneous curvature. The size of the outer radius $r_1$ necessary to avoid finite size effects is determined by the ratio $r_1/\xi_\parallel$. We find that for $r_1/\xi_\parallel > 10$, the dependence of the free energy of the wormhole on $r_1$ becomes negligible. The free energy of a wormhole (relative to a flat membrane) should be independent of the cutoff for $E_c \to \infty$. We determine $E_c$ by the condition that $\langle r_0 \rangle$ should not depend on $E_c$. This gives reasonable results for $E_c \sim 3d^4/(2r_0^4)$. It is therefore necessary to calculate the eigenvalues up to approximately $10E_c$. Figure 4 shows the free energy as a function of the radius $r_0$ of the underlying mean-field conformation, up to an additive constant (which depends on the regularization used in equation (21)).

The results for the size of the wormhole for different bending rigidities (or temperatures) is shown in figure 3. Thermal fluctuations reduce $<r_0>$ compared to the mean-field result. Since $<r_0 > > 0.1$ in the temperature range considered here, which implies a diameter in the center of the wormhole of order 100 Å, microscopic interactions between the membranes in the hole should be negligible. The fluctuations of the radius

$$\Delta r_0 \equiv \left(\langle r_0^2 \rangle - \langle r_0 \rangle^2\right)^{1/2}$$

are about $r_0/2$ (see Fig. 5) and depend only slightly on $\beta \kappa$; they increase with increasing stiffness of the membrane. The reason for this unusual behaviour is again the increase in the steric interaction with decreasing stiffness, which fixes $r_0$ and therefore competes with the increasing thermal fluctuations. We want to point out that, although the result for $\Delta r_0$ shown in figure 5 is very close to the result obtained from Gaussian fluctuations, it now rests on a solid basis.

Another interesting quantity is the shape of the wormhole at $z = 0$. This shape can be characterized by the moment of gyration tensor

$$Q_{ij} = \frac{1}{U} \int_0^{2\pi} d\phi \left[r(\phi)^2 + \left(\frac{d}{d\phi} r(\phi) \right)^2\right]^{1/2} (x_i(\phi)x_j(\phi) - \bar{x}_i \bar{x}_j)$$

(25)
Fig. 4. — Free energy of the wormhole as a function of the radius of the mean-field configuration, for $\kappa/k_B T = 3.0$.

Fig. 5. — Radial fluctuations $\Delta r_0 = (\langle r_0^2 \rangle - \langle r_0 \rangle^2)^{1/2}$ of the radius of a passage, as a function of $\kappa/k_B T$.

with $x_1(\phi) = r(z, \phi) \cos \phi$, $x_2(\phi) = r(z, \phi) \sin \phi$. $\bar{z}_i$ is the $i$-component of the center of mass, and $U$ is the perimeter. We are especially interested in the “asphericity” [32, 33]

$$\langle A_2 \rangle = 2 \frac{\langle \text{tr}(Q^2) \rangle}{\langle (\text{tr}Q)^2 \rangle}$$

(26)

where $\hat{Q} = Q - 1 \text{tr}Q/2$ [34]. Because $A_2$ depends only weakly on $a$, we take in account only the fluctuations of the passage with the mean-field radius $r_0$. The expansion of the asphericity to second order in $k_B T/\kappa$ is given in Appendix C. The numerical results for the mean value $\langle A_2 \rangle$ are shown in figure 6. Again the increase of $A_2$ with increasing stiffness is due to the steric interactions, which allows stronger fluctuations at lower temperatures.

To illustrate our results, and to demonstrate the importance of fluctuations, we show two
typical configurations of the membrane in figure 7. The configurations are obtained by generating amplitudes for the eigenmodes with a Gaussian probability distribution (where the eigenvalue \( E^m \) determines the width of the distribution of amplitudes of eigenmode \( \nu^m \)), and adding all fluctuation modes to the mean-field configuration. Figure 7a shows the whole system; the edge of the membrane is flat due to the boundary conditions (3). More details of the wormhole itself can be seen in figure 7b.

4. Wormholes in systems with spontaneous curvature.

It is well known [35, 36] that the lamellar phase is also stable for small spontaneous curvatures \( H_0 \). Such a situation may occur in an unbalanced ternary mixture of water, oil, and amphiphiles. The phase diagram of such a mixture was calculated in reference [35], with the additional constraints that the area of the membranes and the oil- and water-concentrations are fixed. In this case, the lamellar phase is stable with a spontaneous curvature

\[
|H_0| \leq 1/(8d), \quad (27)
\]

where \( d \) is the (mean) distance between the membranes.

If there are passages between two neighboring membranes the sign of the spontaneous curvature becomes important. A negative \( H_0 \) (in the parametrization of the last two sections) increases the size of a wormhole, while a positive \( H_0 \) makes it smaller. If \( r_0 \) becomes large, we can again neglect terms of order \( 1/r \) in the Lagrangian (4). Then the free energy reads

\[
F = \pi \kappa r_0 \int_0^{\beta} ds \left[ (\psi')^2 - 4H_0\psi' + 4H_0^2 \right]. \quad (28)
\]

It is easily seen that the wormhole becomes unstable if the integral in (28) becomes negative. A numerical analysis of the Euler-Lagrangian equations (7) shows that this happens for \( H_0d < -0.23 \) at \( \beta\kappa = 1.19 \), which is about twice the value (27) of the instability of the lamellar phase as calculated in reference [35]. In an infinite system, the wormhole would transform into a cylinder at this point; in the finite system which we consider, a jump in the size of the passage occurs at this point, which depends on the size of the membranes.
Fig. 7. — Typical configurations of the membrane with fluctuations, for $\kappa/k_B T = 1.19$ and $r_1 = 7.5 \text{ } d$. The pictures are obtained by adding all fluctuations with eigenvalue less than 10 $\kappa$ to the mean-field configurations of the wormhole. The amplitudes are chosen randomly according to their Boltzmann weights. a) Whole membrane; b) The vicinity of the wormhole.

Fig. 8. — Mean radius $\bar{r}_0$ (solid line) and mean-field radius (dashed line) of the wormhole at $\kappa/k_B T = 1.18$ as a function of the spontaneous curvature $H_0 d$.

The mean-field radius of the passage as a function of the spontaneous curvature is shown in figure 8. On the mean-field level, there is no instability for positive $H_0$. The size $r_0$ of the wormhole decreases to about 0.07 $d$ at $H_0 = 1/(5 \text{ } d)$. However, when the fluctuations of the membrane are analysed, an instability is found for $H_0 > 0$ also. For sufficiently large $H_0$, the odd eigenfunction with the lowest eigenvalue becomes a bound state; at $H_0 \approx 1/(7.5 \text{ } d)$ the eigenvalue goes through zero and then becomes negative for large $H_0$. 
Fig. 9. — Radial fluctuations $\Delta r_0 = (\langle \tau_0^2 \rangle - \langle \tau_0 \rangle^2)^{1/2}$ of a passage at $\kappa/k_B T$ as a function of the spontaneous curvature $H_0 d$.

Fig. 10. — Asphericity of the wormhole at $\kappa/k_B T = 1.18$ as a function of spontaneous curvature $H_0 d$. For $A_2 = 1$, the circle is distorted into a line. Thus the sharp increase of the asphericity at positive $H_0$ indicates that the hole becomes more and more elongated.

The radial fluctuations of the wormhole (see Fig. 9) are always smaller than the radius of the hole. But the asphericity of the wormhole, as shown in figure 10, increases rapidly with increasing (positive) spontaneous curvature. Since the radius $r_0$ of the passage remains small, membrane collisions in the inner part of the wormhole will probably become important near the instability; thus, we are leaving the range of validity of our model.

5. Summary and conclusions.

Shape and fluctuations of a passage between neighboring membranes in a lamellar phase have been studied in a model based on the elastic curvature Hamiltonian. In order to include effects of self-avoidance, we have introduced an effective potential, which describes the steric
interaction of the membranes caused by collisions. We found that this potential stabilizes wormholes of finite radius $r_0$, which is of the order $0.15d$.

The effects of thermal fluctuations have been calculated in the capillary wave approximation. We find that there are large fluctuations in the radius of the wormhole, which were treated exactly. Furthermore, we have determined the thermal average of the asphericity, which measures the deviation of a $z = 0$ - cut through the wormhole from a circle. The mean size of a wormhole and its fluctuations as well as the asphericity can be extracted from pictures of lamellar phases obtained by freeze fracture microscopy [16]. Thus, we hope that a quantitative comparison of our results with experiments will be possible in the near future.

Finally, we have determined the influence of spontaneous curvature on the size and stability of wormholes. We found an instability at a negative spontaneous curvature, where the lamellar phase becomes energetically unstable to a phase of cylinders. This instability occurs in a region where the lamellar phase is already metastable. Another instability occurs at positive spontaneous curvature, which is due to diverging fluctuations. This instability occurs roughly at the same point where the lamellar phase becomes metastable. Therefore, wormholes may play an important role at the transition from the lamellar phase to the hexagonal phase of cylindrical micelles.

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**Appendix A. Expansion of the curvature energy.**

The expansion to second order in the fluctuations gives for the curvature energy [37]

$$
(2H)^2 = 4(H_{mf} - H_0)^2 + 4(H_{mf} - H_0)\nabla^2 \nu - \left[8(H_{mf}^2 - K_{mf})H_{mf} + 4H_0K_{mf} - 2H_0^2H_{mf}\right] \nu + (\nabla^2 \nu)^2 - \\
\left[4(H_{mf} - H_0)(C^{ij} - H_{mf}g^{ij}_0) + g^{ij}_0 \left(6H_{mf}^2 - 4K_{mf} - 4H_{mf}H_0 + 2H_0^2\right)\partial_i \nu \partial_j \nu + \\
16H_{mf}^4 - 20H_{mf}^2K_{mf} + 4K_{mf}^2\nabla^2(4H_{mf}^2 - 2K_{mf}) + 4\nabla_j \left(\partial_i (H_{mf} - H_0) \left(C^{ij} - H_0g^{ij}_0\right)\right)\nu^2
\right]
$$

(29)

where $H_{mf}$, $K_{mf}$ are the mean and Gaussian curvature of the mean-field conformation, and $g^{ij}_0$ and $C^{ij}$ are the first and second fundamental forms in this geometry, respectively. $\nabla$ denotes the covariant derivative.

**Appendix B. Expansion of the effective potential.**

In this appendix we want to calculate the expansion of the effective potential $V_{eff}$ around the mean-field solution $X_0$, $V_{eff}(X_0 + \nu n_0)$, where $n_0$ is the normal vector on $X_0$. Due to the rotational symmetry of our problem, we can use the expansion (20). Therefore we have to expand

$$
g^{1/2}V_{eff}(X_0(s, \phi) + \nu_0(s) \cos m\phi n_0(s, \phi) = g^{1/2}_0(V_{eff}(X_0) + B_1^m\nu_0 + \nu_0 B_2^m\nu_0),
$$

(30)
where $B_{1/2}^m$ are differential operators, $g$ and $g_0$ are the metrics of the fluctuating membrane and of the mean-field conformation, respectively. Because we expand around a solution which minimizes the Hamiltonian, we only need the coefficients $B_{1/2}^m$. The normal vector on $X_a$ is given by

$$n_a(s, \phi) = (-\sin \psi_{mf}(s) \cos \phi, -\sin \psi_{mf}(s) \sin \phi, \cos \psi_{mf}(s))$$  \hspace{1cm} (31)$$

where $\psi_{mf}$ is the tangent angle of the mean-field shape. Special care has to be taken in the expansion of the tangent angle $\psi$. Because $s$ is no longer the correct arc-length of the fluctuating membrane, the equations $s' = \sin \psi$ and $r' = \cos \psi$ do not hold. The correct expansion of $\psi$ leads to

$$\tan \psi = \frac{\sin \psi_{mf} + \nu \psi'_{mf} \cos \psi_{mf} + \nu' \sin \psi_{mf}}{\cos \psi_{mf} + \nu \psi'_{mf} \sin \psi_{mf} - \nu' \cos \psi_{mf}}.$$  \hspace{1cm} (32)$$

Then, after some algebra, we find

$$B_{2}^m = \frac{d_4}{4 \xi_4} \left\{ \left( \frac{z_{2}^m}{d^2} - \frac{1}{4} \right)^2 \left[- \cos^2 \psi_{mf} \left( \frac{m^2}{8 r_{mf}^2} - \frac{\psi_{mf} \sin \psi_{mf}}{2 r_{mf}} \right)^2 + \psi'_{mf} \sin \psi_{mf} \right] \right. $$

$$- \cos \psi_{mf} \sin^2 \psi_{mf} \left( \frac{z_{2}^m}{d^2} - \frac{1}{4} \right) \left[ \frac{2 \psi'_{mf} + \sin \psi_{mf}}{r_{mf}} \right] - \frac{1}{2} \left( \sin^4 \psi_{mf} - 1 \right) \left( 3 z_{2}^m - 1 \right) $$

$$+ \frac{1}{8} \left( \frac{z_{2}^m}{d^2} - \frac{1}{4} \right)^2 \left[ \cos \psi_{mf} \left( 1 - 3 \sin^2 \psi_{mf} \right) - 6 \psi'_{mf} \cos \psi_{mf} \sin \psi_{mf} \right]$$

$$+ 4 \left( \frac{z_{2}^m}{d^2} - \frac{1}{4} \right) \sin \psi_{mf} (1 - 3 \sin^2 \psi_{mf}) \partial_s + \frac{1}{8} \left( \frac{z_{2}^m}{d^2} - \frac{1}{4} \right)^2 (1 - 3 \sin^2 \psi_{mf}) \partial_s^2 \right\}.$$  \hspace{1cm} (33)$$

Here the index "mf" again denotes functions describing the mean-field shape of the passage.

**Appendix C. Expansion of the asphericity.**

First we want to calculate the gyration tensor (25) in terms of the expansion coefficients $\alpha_i^m$, $\beta_i^m$ of equation (20). With the definitions

$$u_m = \sum_i \alpha_i^m \nu_i^m(0)$$ \hspace{1cm} (34)$$

$$v_m = \sum_i \beta_i^m \nu_i^m(0)$$

and equation (31) we can write

$$r(s = 0, \phi) = r_{mf} - \sum_m (u_m \cos m \phi + v_m \sin m \phi).$$  \hspace{1cm} (35)$$

Insertion of this expansion in (25) yields

$$Q_{11} = \frac{1}{2} r_g + \Delta$$

$$Q_{22} = \frac{1}{2} r_g - \Delta$$  \hspace{1cm} (36)$$

with the square of the radius of gyration

$$r_g^2 = r_{mf}^2 - 2 r_{mf} u_0 + u_0^2 + \frac{1}{2} (u_1^2 + v_1^2) + \frac{3}{2} \sum_{n=2}^\infty (u_n^2 + v_n^2).$$  \hspace{1cm} (37)$$
\[ \Delta = \frac{3}{4} u_2 (u_0 - r_m) - \frac{3}{16} (u_1^2 - v_1^2) + \frac{1}{8} \sum_{n=1}^{\infty} \left( 6 + n(n + 2) \right) (u_n u_{n+2} + v_n v_{n+2}). \]  

(38)

For \( Q_{12} \) we get

\[ Q_{12} = \frac{3}{4} v_2 (u_0 - r_m) - \frac{3}{8} u_1 b_1 + \frac{1}{8} \sum_{n=1}^{\infty} \left( 6 + n(n + 2) \right) (u_n u_{n+2} - v_n v_{n+2}). \]  

(39)

After calculating the traces and doing the thermal averages, we finally arrive at

\[
\langle \text{tr}(Q^2) \rangle = \langle \Delta^2 + Q_{12}^2 \rangle = \frac{9}{8} r^2 \langle u_2^2 \rangle - \frac{3}{4} r (u_0) \langle u_2^2 \rangle + \frac{9}{128} (\langle u_1^4 \rangle + \langle u_2^4 \rangle)^2 + \frac{9}{8} \langle u_0^2 \rangle \langle u_2^2 \rangle + \frac{1}{16} \sum_{m=1}^{\infty} (6 + m(m + 2))^2 \langle u_m^2 \rangle \langle u_{m+2}^2 \rangle
\]  

(40)

and

\[
\frac{1}{2} \langle (\text{tr}Q)^2 \rangle = \frac{1}{4} \langle r_4^4 \rangle = \frac{1}{4} r^4 - r^3 \langle u_0 \rangle - r \langle u_0^3 \rangle - r \langle u_0 \rangle \left[ \langle u_1^2 \rangle + 3 \sum_{m=2} \langle u_m^2 \rangle \right] + r^2 \left[ \frac{3}{2} \langle u_0^2 \rangle + \frac{1}{2} \langle u_2^2 \rangle + \frac{3}{2} \sum_{m=2} \langle u_m^2 \rangle \right] + \frac{1}{4} \langle u_0^4 \rangle + \frac{9}{8} \left[ \langle u_1^4 \rangle + \langle u_2^4 \rangle \right] + \frac{9}{2} \sum_{m=2} \langle u_m^4 \rangle + \frac{1}{2} \langle u_0^2 \rangle \langle u_2^2 \rangle + \frac{3}{2} \left[ \langle u_0^2 \rangle + \frac{1}{2} \langle u_2^2 \rangle \right] \sum_{m=2} \langle u_m^2 \rangle + \frac{9}{2} \sum_{m=2} \langle u_m^2 \rangle \langle u_{m+2}^2 \rangle
\]  

(41)

\( \langle u_0 \rangle \) and \( \langle u_0^3 \rangle \) do not vanish, because of the term linear in \( v \) introduced by the Faddeev-Popov determinant. Thus the averages \( \langle u_m^2 \rangle \) are given by

\[
\langle u_m \rangle = \frac{1}{2 \beta} \sum_{i} \frac{L_i^m \nu_i^m(0)}{E_i^m}
\]

\[
\langle u_2^m \rangle = \frac{1}{2 \beta} \sum_{i} \frac{(\nu_i^m(0))^2}{E_i^m} + \frac{1}{4 \beta^2} \sum_{ij} \frac{L_{ij}^m L_{ij}^m \nu_i^m(0) \nu_j^m(0)}{E_i^m E_j^m}
\]

\[
\langle u_3^m \rangle = -3 \frac{1}{4 \beta^2} \sum_{i} \frac{L_{i}^m (\nu_i^m(0))^3}{(E_i^m)^2} + O((\beta \kappa)^{-3})
\]

(42)

\[
\langle u_4^m \rangle = \frac{3}{4 \beta^2} \sum_{ij} \frac{(\nu_i^m(0) \nu_j^m(0))^2}{E_i^m E_j^m} + O((\beta \kappa)^{-3}).
\]

References


[27] DAVID F., in Reference [2].


[30] Due to this condition, the number of eigenvalues we have to calculate for $\beta \kappa = 3.0$ is about 1600 for fixed $r_0$. The integral (13) is calculated by evaluating the integrand at 12 different points.

[31] Due to the enormous number of eigenvalues necessary we could not do any calculations for $\beta \kappa > 5$.


[34] For simplicity we calculate the thermal average of $A_2$ by doing separately the average of the numerator and the denominator of $A_2$.

