

Preferred configurations of linear polymers embedded in planar membranes under lateral tension

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We consider a linear polymer in a flat membrane exposed to a lateral tension γ_0 . The polymer is assumed to produce a sharp bend in the membrane so that in its straight state it gives rise to a symmetric ridge of width $\lambda = \sqrt{\kappa/\gamma_0}$, κ being the bending rigidity of the membrane. We calculate the effective in-plane bending energy of the polymer that originates from the deformation of the membrane ridge. The parameter controlling the energy as a function of curvature of the polymer is $\Delta\bar{\kappa}/\kappa$, where $\Delta\bar{\kappa}$ is the difference of the moduli of Gaussian curvature of unpolymerized and polymerized lipid. Depending on its value, the presence of the ridge increases the persistence length or destabilizes the straight configuration of the polymer. Destabilization occurs on both sides of a range of stability, leading in the case of circular configurations to craters with a depressed or elevated interior.

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INTRODUCTION

Fluid lipid membranes with inclusions model biological membranes consisting of a lipid matrix with incorporated proteins. A special kind of such inclusions are cross-linked or linear polymers spread in the membrane as in a two-dimensional solution. They can be produced by uv irradiation of bilayers containing a polymerizable lipid [1–6]. Also, water soluble polymers can be anchored to the bilayer surface if they contain groups with one or two long alkyl chains [1]. Cross-linked polymerization was found to produce a very strong wrinkling of the bilayers [2–4], while linear polymerization linking up to 10^4 monomers resulted in the formation of bulges and buds on vesicle membranes [5]. Evidently, both kinds of polymers are capable of producing a spontaneous curvature in an initially flat, symmetric bilayer.

In theoretical work, we recently considered the effect of linear polymers treated as two-dimensional self-avoiding random walks on the bending elasticity of fluid membranes [7,8]. We also studied the interaction of linear polymers with tethers, i.e., thin bilayer tubes pulled from vesicles, showing that polymers may align parallel to the tether and thus deform its cross section [9].

The interaction of polymer configuration and membrane shape is a complicated problem which has to be solved step by step. So far, we have assumed the polymer to be a continuous sequence of loosely linked monomers, all in the same monolayer. The persistence length of such a chain equals the distance between subsequent constituents. The linked monomers were taken to differ from single monomers only in their local monolayer spontaneous curvature.

If for some reason such a polymer is straight it gives rise to a sharp bend of the bilayer along the line where it is embedded. The result would be a roof (or a V-shaped valley) in the case of an unstressed bilayer. The molecular basis for such a shape is considered in detail in the Appendix. When a lateral tension tends to keep the

membrane flat, the straight polymer will be at the peak of a membrane ridge (or at the bottom of a furrow) the sides of which gradually bend into the plane of the undisturbed membrane.

The present paper deals with the effective energy of the in-plane bending of the linear polymer that arises from the bending elasticity of the membrane forming the ridge. Any elasticity of the polymer backbone is omitted in the following calculations, in accordance with a loosely linked chain.

A single polymer is considered which is assumed to be uniformly curved in the plane of the membrane. Neglecting fluctuations, we find either the straight configuration or circles to have the lowest free energy per unit length of the polymer. We also derive the effective bending stiffness for the straight configuration. An estimate suggests that it can lead to a dramatic increase of the persistence length of the polymer. While the ridge is symmetric for the straight polymer, it is in general tilted for circular configurations. We will show that the central parameter controlling tilt and curvature of minimum energy is $\Delta\bar{\kappa}/\kappa$. In this ratio, κ is the bending rigidity of the nonpolymerized surfactant, and $\Delta\bar{\kappa}$ the difference of the moduli of Gaussian curvature between unpolymerized and polymerized material. The circular ridges resemble craters with a depressed or elevated center, depending on whether the tilt is inward or outward. Prevented from splitting up into circles, a long polymer chain may instead be expected to curl up into many loops.

MODEL

We consider a single polymer embedded in a symmetric bilayer. The flat bilayer is exposed to a lateral tension $\gamma_0 > 0$. Deviations of the membrane from the flat state are expected only in a vicinity of the polymer, their decay length $\lambda = \sqrt{\kappa/\gamma_0}$ (see below) being controlled by the interplay of lateral tension and bending elasticity.

The polymer may be a chain of polymerized surfactant

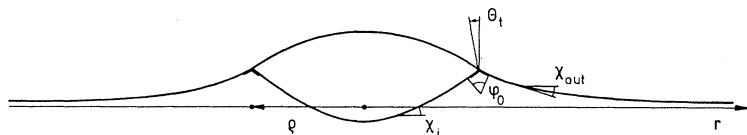


FIG. 1. Circular ridge formed by polymer in an otherwise flat membrane exposed to lateral tension.

molecules in one of the monolayers or a hydrophilic chain anchored at regular intervals on one side of the membrane. The polymerized surfactant molecules or the surfactant molecules anchoring the chain will, as a rule, produce a local spontaneous curvature in the otherwise symmetric bilayer. Accordingly, each of the surfactant molecules belonging to the polymer forms a hat and the polymer chain forms a ridge in the membrane. The angle φ_0 by which the membrane bends at the top of the ridge will be called ridge angle. For simplicity, this angle is assumed to be sharp, uniform, and insensitive to lateral tension in the following calculations.

Actually, the bend of the top of the ridge is spread over a molecular width along a continuous chain of polymerized surfactant molecules. Moreover, the cross section of a ridge resulting from separate anchoring molecules is nonuniform even when they are regularly spaced. Inspection shows the uniform approximation to be justified for regular spacing when the decay length λ and the radius of polymer in-plane curvature are much larger than the spacing of the anchors.

The bending elasticity of a symmetric bilayer is characterized by its bending rigidity κ and vanishing spontaneous curvature [10]. The modulus of Gaussian curvature $\bar{\kappa}$ does not enter if the bilayer retains its topology and is homogeneous. The second condition is violated when a different value of the modulus $\bar{\kappa}_p$ holds for the surfactant molecules belonging to the polymer. The difference between the moduli of Gaussian curvature $\Delta\bar{\kappa} = \bar{\kappa} - \bar{\kappa}_p$ will be an important quantity in the following. The value of the bending rigidity of the polymerized molecules should not matter as they form a very narrow strip which is in its spontaneously curved state. The contribution of the strip to the regular bending energy (κ term) seems negligible except for very high curvatures of the polymer.

We want to calculate the total bilayer bending energy per unit length of membrane ridge, considering polymers which can be straight or uniformly curved in the plane of the bilayer. For simplicity, the curved polymers are taken to be closed rings of radius ρ . Another property characterizing the conformation of the system is a tilt of the ridge with respect to the plane of the flat bilayer. The tilt angle θ_t , defined by Fig. 1, is counted positive for outward tilt. While straight ridges are always symmetric ($\theta_t = 0$) in the state of minimum energy, we will find circular ridges to display as a rule outward or inward tilt.

PROBLEM AND MAIN EQUATIONS

The free energy per unit area of curved bilayer may be written as

$$\gamma = \gamma_0 + \frac{1}{2}\kappa J^2 + \bar{\kappa}K, \quad (1)$$

where $J = c_1 + c_2$ and $K = c_1 c_2$ are the total and Gaussian curvatures, respectively, c_1 and c_2 being the principal curvatures. This quantity is the sum of the lateral tension γ_0 of the flat membrane and the bending tensions in their usual form. The total free energy can be calculated by integrating (1) over the membrane area

$$F = \int \gamma dA. \quad (2)$$

To determine F for a circular membrane ridge (Fig. 1) we need to know the dependences of the curvatures on the radial coordinate r , i.e., $J(r)$ and $K(r)$. The total curvature can be found from the equilibrium equation [11]

$$\frac{d^2 J}{dr^2} + \frac{1}{r} \frac{dJ}{dr} - \frac{\gamma_0}{\kappa} J = 0, \quad (3)$$

which neglects all terms of higher than linear order in the curvatures. Note that generally $\bar{\kappa}$ terms drops out of shape equations. Both the total curvature and the Gaussian curvature can be expressed by the gradient angle χ of the membrane contour (see Fig. 1). To lowest order we have

$$J = \frac{d\chi}{dr} + \frac{\chi}{r} \quad (4)$$

and

$$K = \frac{\chi}{r} \frac{d\chi}{dr}. \quad (5)$$

Equations (3) and (5) are valid for $|\chi| \ll 1$ or, equivalently, $|J| \ll 1/r$.

MEMBRANE SHAPE

Considering a circular polymer of radius ρ , we solve the equilibrium Eq. (3) for the membrane inside and outside of the circle of radius ρ (Fig. 1) and distinguish the respective quantities by subscripts *in* and *out*. The boundary conditions for (3) are conveniently expressed by the gradient angle χ which becomes zero at large radii, $\chi_{out}(r \rightarrow \infty) = 0$, and at the center of the circle, $\chi_{in}(r = 0) = 0$, in the latter case because of rotational symmetry. Moreover, the two values of the gradient angle at the circle are related to the ridge angle through

$$\chi_{in}(r = \rho) - \chi_{out}(r = \rho) = \varphi_0. \quad (6)$$

The tilt angle θ_t , as yet a free parameter, can be expressed by

$$\chi_{in}(r = \rho) + \chi_{out}(r = \rho) = -2\theta_t. \quad (7)$$

Solving first (3) and then (4) with the respective boundary conditions and using (6) and (7), we obtain [12]

$$J_{\text{in}} = \frac{(\frac{1}{2}\varphi_0 - \theta_t)}{\lambda} \frac{I_0(r/\lambda)}{I_1(\rho/\lambda)}, \quad (8)$$

$$\chi_{\text{in}} = (\frac{1}{2}\varphi_0 - \theta_t) \frac{I_1(r/\lambda)}{I_1(\rho/\lambda)}, \quad (9)$$

and

$$J_{\text{out}} = \frac{(\frac{1}{2}\varphi_0 + \theta_t)}{\lambda} \frac{K_0(r/\lambda)}{K_1(\rho/\lambda)}, \quad (10)$$

$$\chi_{\text{out}} = -(\frac{1}{2}\varphi_0 + \theta_t) \frac{K_1(r/\lambda)}{K_1(\rho/\lambda)}. \quad (11)$$

Here $\lambda = \sqrt{\kappa/\gamma_0}$ is the characteristic length determining the decay of deviations of the membrane from the flat state, while $I_0(r/\lambda)$, $I_1(r/\lambda)$, $K_0(r/\lambda)$, and $K_1(r/\lambda)$ are modified Bessel functions [12].

MEMBRANE FREE ENERGY

To calculate the free energy of the membrane we integrate according to (2) the lateral tension (1) over the membrane surface, employing (8)–(11), and subtract the free energy of the flat membrane (which is γ_0 times the area of the flat membrane). The resulting free energy per unit length of polymer is

$$f = \frac{1}{2} \frac{\kappa}{\lambda} \frac{I_0(\rho/\lambda)}{I_1(\rho/\lambda)} (\frac{1}{2}\varphi_0 - \theta_t)^2 + \frac{1}{2} \frac{\kappa}{\lambda} \frac{K_0(\rho/\lambda)}{K_1(\rho/\lambda)} (\frac{1}{2}\varphi_0 + \theta_t)^2 - \frac{\Delta\bar{\kappa}}{\rho} \phi_0 \theta_t. \quad (12)$$

Alternatively, the first and second terms of (12) can be derived directly by integrating the work of the bending moment $\kappa J d\chi$ done at the circle on the inner and outer parts of the membrane, respectively. The third term can be obtained directly from ρ , θ_t , and φ_0 on the assumption that $|\varphi_0|, |\theta_t| \ll 1$. Minimizing (12) with respect to the tilt angle θ_t , we find the equilibrium value

$$\theta_t = \frac{1}{2} \varphi_0 \frac{\frac{I_0(\rho/\lambda)}{I_1(\rho/\lambda)} - \frac{K_0(\rho/\lambda)}{K_1(\rho/\lambda)} + 2 \frac{\Delta\bar{\kappa}\lambda}{\kappa\rho}}{\frac{I_0(\rho/\lambda)}{I_1(\rho/\lambda)} + \frac{K_0(\rho/\lambda)}{K_1(\rho/\lambda)}}. \quad (13)$$

Inserting this in (12) leads to the final formula for the energy per unit length

$$f = \frac{1}{2} \varphi_0^2 \sqrt{\gamma_0 \kappa} \frac{\left[\frac{I_0(\rho/\lambda)}{I_1(\rho/\lambda)} + \frac{\Delta\bar{\kappa}\lambda}{\kappa\rho} \right] \left[\frac{K_0(\rho/\lambda)}{K_1(\rho/\lambda)} - \frac{\Delta\bar{\kappa}\lambda}{\kappa\rho} \right]}{\left[\frac{I_0(\rho/\lambda)}{I_1(\rho/\lambda)} + \frac{K_0(\rho/\lambda)}{K_1(\rho/\lambda)} \right]}. \quad (14)$$

The last two equations permit us to calculate θ_t and f as functions of the circle radius ρ .

STRAIGHT POLYMER

First, let us consider the stability of straight configuration of the polymer ($1/\rho \rightarrow 0$). The expansion

of (14) up to the first nonvanishing order in $1/\rho$ gives

$$f = \frac{1}{4} \varphi_0^2 \sqrt{\gamma_0 \kappa} \left[1 + \left[\frac{3}{8} - \left[\frac{1}{2} + \frac{\Delta\bar{\kappa}}{\kappa} \right]^2 \right] \frac{\lambda^2}{\rho^2} \right]. \quad (15)$$

Defining an effective in-plane bending stiffness of the polymer μ_p through the formula

$$f = f_0 + \frac{1}{2} \mu_p \frac{1}{\rho^2},$$

where $f_0 = \frac{1}{4} \varphi_0^2 \sqrt{\gamma_0 \kappa}$ is the free energy of the straight ridge, we obtain from (15)

$$\mu_p = \frac{1}{2} \varphi_0^2 \left[\frac{\kappa^3}{\gamma_0} \right]^{1/2} \left[\frac{3}{8} - \left[\frac{1}{2} + \frac{\Delta\bar{\kappa}}{\kappa} \right]^2 \right]. \quad (16)$$

The dimension of μ_p is energy times length, while that of κ is energy. As long as μ_p is positive, the straight configuration of the polymer represents an energy minimum. It will be shown below that the minimum can be absolute or local. The sign of μ_p is determined by the ratio $\Delta\bar{\kappa}/\kappa$ introduced above. Evidently, μ_p is positive as long as $\Delta\bar{\kappa}/\kappa$ is within the limits

$$-\frac{1}{2}(\sqrt{3/2} + 1) \leq \frac{\Delta\bar{\kappa}}{\kappa} \leq \frac{1}{2}(\sqrt{3/2} - 1). \quad (17)$$

If $\Delta\bar{\kappa}/\kappa$ is not in the range (17), the straight configuration of the polymer is absolutely unstable and the chain tends to bend in the plane of the membrane. We will come back to curved equilibrium states later on.

Even if the bending stiffness of the polymer is positive $\mu_p > 0$ the straight configuration will be disturbed by thermal fluctuations. Such fluctuations may destroy directional correlation and result in a mean square end-to-end distance R_F (Flory radius) of the chain much smaller than its total length. The value of R_F is governed by the number N of independent persistence lengths into which the polymer can be divided, obeying $R_F = \xi N^\nu$, where ξ is the persistence length and ν is a known exponent [13]. The stiffer the chain, the larger is ξ and the smaller is N . The persistence length of the chain in the absence of a ridge is equal to the dimension of one monomer which for a membrane polymer is $\xi_0 \approx 0.8$ nm (diameter of the lipid polar head in the plane of the membrane).

The presence of a membrane ridge increases the persistence length to a value ξ_μ . Employing a well-known formula and assuming $\xi_\mu \gg \xi_0$, we find the persistence length to be $\xi_\mu = \mu_p/kT$, where kT is the product of Boltzmann constant and absolute temperature. Dropping numerical factors, one obtains from (16) the approximate formula

$$\xi_\mu = \frac{\varphi_0^2}{kT} \sqrt{\kappa^3/\gamma_0}. \quad (18)$$

For an estimate, which may be appropriate to partially polymerized lipid membranes, we assume $\varphi_0 = 0.1$, $\kappa = \frac{2}{3} 10^{-19}$ J (a value typical of lipid bilayers [14]) and $\gamma_0 = 10^{-6}$ J/m² [15]. This combination leads to $\xi_\mu \approx 10$ nm, which is considerably larger than the value ξ_0 valid for $\varphi_0 = 0$. It means that the stiffening due to the ridge

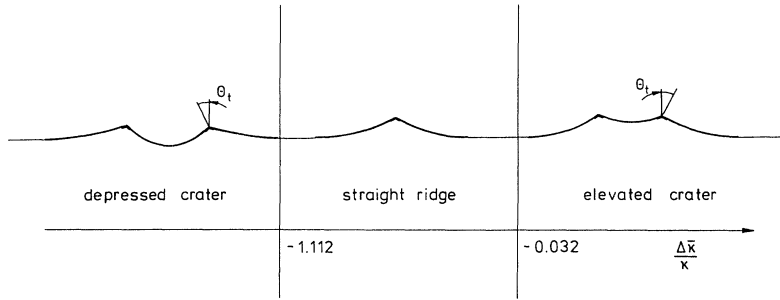


FIG. 2. Shapes of the membrane for different tilt angles θ_i of the ridge. (1) θ_i is negative, depressed crater; (2) θ_i is zero, straight ridge; (3) θ_i is positive, elevated crater. The horizontal line represents the phase diagram of the system.

can strongly expand the Flory radius of the polymer. If the parameters of the system are such that the persistence length ξ_μ is larger than the total length of the chain, the polymer will be straight.

The tilt angle of the straight configuration of the polymer is always zero, $\theta_i = 0$. This follows from symmetry and can also be seen by inserting zero polymer curvature $1/\rho = 0$ into (13). The membrane ridge then has a symmetric shape as illustrated by Fig. 2.

BENT POLYMER: DEPRESSED AND ELEVATED CRATERS

Depressed craters. If $\Delta\bar{\kappa}/\kappa$ is not in the interval (17), the straight configuration of the polymer is unstable. We consider first what happens if $\Delta\bar{\kappa}/\kappa$ becomes smaller than the lower limit of (17),

$$\left[\frac{\Delta\bar{\kappa}}{\kappa} \right]_1 = -\frac{1}{2}(\sqrt{3/2} + 1) \simeq -1.112.$$

Figure 3 shows the energy f as a function of the dimensionless polymer curvature $\sqrt{\kappa/\gamma_0}(1/\rho)$ for the parameter $\Delta\bar{\kappa}/\kappa$ near $(\Delta\bar{\kappa}/\kappa)_1$. In each curve there is a curvature of minimal energy which should not be confused with a spontaneous curvature as the sign of this curvature is irrelevant. The curvature of minimal energy is zero for $\Delta\bar{\kappa}/\kappa > (\Delta\bar{\kappa}/\kappa)_1$ and nonzero for $\Delta\bar{\kappa}/\kappa < (\Delta\bar{\kappa}/\kappa)_1$. The transition of the curvature of

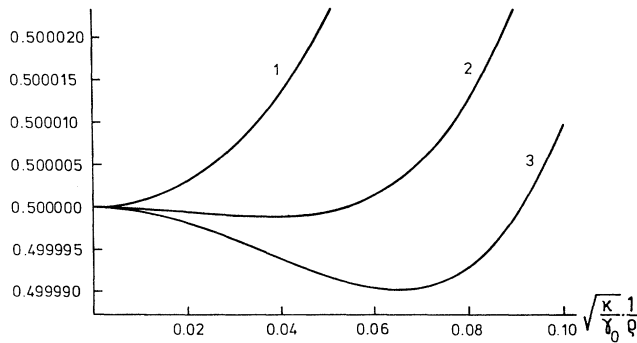


FIG. 3. Dimensionless energy per unit length of polymer, $(2/\varphi_0^2\sqrt{\gamma_0\kappa})f$, versus dimensionless in-plane curvature $\sqrt{\kappa/\gamma_0}(1/\rho)$ for different values of the control parameter $\Delta\bar{\kappa}/\kappa$ near $(\Delta\bar{\kappa}/\kappa)_1 \simeq -1.112$. (1) $(\Delta\bar{\kappa}/\kappa) = -1.100$; (2) $(\Delta\bar{\kappa}/\kappa) = -1.115$; (3) $(\Delta\bar{\kappa}/\kappa) = -1.12$.

minimal energy to nonzero values as illustrated in Fig. 3 has the character of a second order phase transition, with $\Delta\bar{\kappa}/\kappa$ being the control parameter. To obtain the equilibrium curvature as a function of the control parameter near the phase transition point we expand f up to fourth order in $1/\rho$,

$$f = \frac{1}{4}\varphi_0^2\sqrt{\gamma_0\kappa} \left\{ 1 + \left[\frac{3}{8} - \left[\frac{1}{2} + \frac{\Delta\bar{\kappa}}{\kappa} \right]^2 \right] \frac{\lambda^2}{\rho^2} + \frac{3}{8} \left[\left[\frac{\Delta\bar{\kappa}}{\kappa} - \frac{1}{2} \right]^2 + \frac{5}{16} \right] \frac{\lambda^4}{\rho^4} \right\}. \quad (19)$$

Minimization of this energy yields

$$\frac{1}{\rho} \simeq 0.75\sqrt{\gamma_0/\kappa} \left[\left[\frac{\Delta\bar{\kappa}}{\kappa} \right]_1 - \frac{\Delta\bar{\kappa}}{\kappa} \right]^{1/2}, \quad (20)$$

i.e., the curvature of minimum energy depends on the relative control parameter with the critical exponent equal to $\frac{1}{2}$.

Inspection of (13) shows that the equilibrium tilt angle θ_i , being zero in the straight configuration, undergoes a transition to nonzero values together with the curvature. Near the phase transition, it obeys

$$\theta_i \simeq -0.23\varphi_0 \left[\left[\frac{\Delta\bar{\kappa}}{\kappa} \right]_1 - \frac{\Delta\bar{\kappa}}{\kappa} \right]^{1/2}. \quad (21)$$

A negative θ_i means in our definition that the ridge tilts towards the inside of the circle. As a result, the polymer ring, if not too small, produces a depressed crater in the otherwise flat bilayer (Fig. 2). The more negative $\Delta\bar{\kappa}/\kappa - (\Delta\bar{\kappa}/\kappa)_1$, the deeper is the crater.

Elevated craters. We consider next the transition from the straight configuration of the polymer to the bent one that takes place when $\Delta\bar{\kappa}/\kappa$ approaches the upper limit of the interval (17), $(\Delta\bar{\kappa}/\kappa)_2 \simeq 0.112$. Figure 4 shows the dependence of the energy f on the dimensionless curvature $\sqrt{\kappa/\gamma_0}(1/\rho)$ for different parameters $\Delta\bar{\kappa}/\kappa$. Having at low enough $\Delta\bar{\kappa}/\kappa$ only the minimum at $1/\rho = 0$ [Fig. 4 (curve 1)], the energy develops a second minimum in a bent configuration as the control parameter passes about -0.05 [Fig. 4 (curve 2)]. The energy at the second minimum becomes equal to the energy of the straight configuration when $\Delta\bar{\kappa}/\kappa$ reaches the special value

$$\left[\frac{\Delta\bar{\kappa}}{\kappa} \right]_3 \simeq -0.032. \quad (22)$$

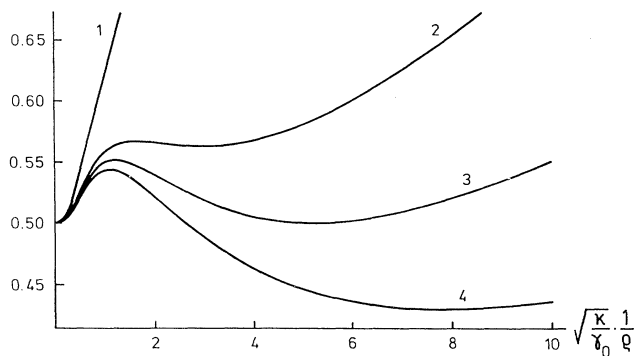


FIG. 4. Dimensionless energy per unit length of polymer, $(2/\varphi_0^2\sqrt{\gamma_0\kappa})f$, versus dimensionless in-plane curvature for different values of the control parameter $\Delta\bar{\kappa}/\kappa$, near $(\Delta\bar{\kappa}/\kappa)_3 \approx -0.032$. (1) $(\Delta\bar{\kappa}/\kappa) = -0.2$; (2) $(\Delta\bar{\kappa}/\kappa) = -0.05$; (3) $(\Delta\bar{\kappa}/\kappa) = -0.032$ (transition value); (4) $(\Delta\bar{\kappa}/\kappa) = -0.02$.

At higher values of $\Delta\bar{\kappa}/\kappa$ the bent configuration is energetically more favorable than the straight one [Fig. 4 (curve 4)]. The special value of the control parameter (22) marks a first-order phase transition. The curvature of minimal energy jumps at the transition point from 0 to

$$\frac{1}{\rho} \approx 5.2\sqrt{\gamma_0/\kappa}. \quad (23)$$

The tilt angle changes at the transition from zero to

$$\theta_t \approx 0.9\varphi_0. \quad (24)$$

The positive value of θ_t in the new state means that the ridge is tilted outwards. In this case the polymer forms an elevated crater in the otherwise flat membrane. The larger the control parameter $\Delta\bar{\kappa}/\kappa$, the sharper is the crater and the higher is its center. The straight configuration remains, of course, locally stable up to $(\Delta\bar{\kappa}/\kappa)_2$.

DISCUSSION

Our theory started from the notion that a polymer chain produces a ridge when it is embedded in one side of a bilayer that is stretched flat by a lateral tension. We calculated the bending energy of the membrane ridge per unit length of curved polymer. This was done for closed circles and the ridge was allowed to tilt outward or inward to assume the angle of minimum energy. The results show that if length is measured in units of λ , the decay length of deviation from membrane flatness, the in-plane polymer curvature of minimum energy depends solely on the ratio $\Delta\bar{\kappa}/\kappa$. We recall that $\Delta\bar{\kappa} = \bar{\kappa} - \bar{\kappa}_p$ is the modulus of Gaussian curvature of unpolymerized lipid minus that of polymerized lipid.

The straight configuration was found to be locally stable in a range of $\Delta\bar{\kappa}/\kappa$ including zero. Surprisingly, the range of absolute stability of the straight configuration is restricted to negative values of $\Delta\bar{\kappa}/\kappa$ and

does not extend up to zero. This result has to be regarded with caution, because in our model a long polymer chain is, in effect, decomposed into noninteracting circles, while the real chain is continuous. We cannot conceive of a pattern of loops with an energy per unit length as low as in widely separated circles. This is because the hats produced by the elements of a continuous chain tend to repel each other. We suspect that for long chains the straight configuration is absolutely stable up to the limit of local stability.

According to our estimate, a loosely linked polymer embedded in a lipid bilayer can have a considerable persistence length which varies with the square of a ridge angle. This agrees with our previous estimate that the thermal fluctuations of a polymer embedded in one side of a bilayer tether do not prevent a good alignment of the polymer parallel to the tether [9]. Such an alignment requires, of course, that the ridge is directed outward and has a sufficient angle. However, the present work also suggests that above some very large $\Delta\bar{\kappa}/\kappa$ the polymer may prefer to spiral around the tether.

Whenever $\Delta\bar{\kappa}/\kappa$ is outside the range (7) where the straight state is locally (and perhaps generally) stable, the polymer may be expected to curl up. This should result in a pattern of nonintersecting loops which seems extremely difficult to predict. The size of the loops could reach the order of the size of the persistence length in the absence of a ridge. One may wonder whether or not the curling of linear polymers produces a wrinkling of the membrane. This problem can be handled only by a theory that goes beyond the approximation of small gradient angles.

CONCLUDING REMARKS

The present calculations show that the membrane ridge caused by an embedded polymer in a stretched membrane can have two very different effects on the configuration of the polymer. The ridge either increases the persistence length of the polymer or makes it curl up into an unknown pattern of loops. We did not consider the interaction of different polymers through their ridges in a stretched membrane. Such interaction is repulsive in our case, but can be attractive as well, e.g., between a ridge and a furrow. Other molecular interactions in mixed membranes are equally disregarded, e.g., those mediated by membrane curvature and its fluctuations [16] or by perturbations of the membrane thickness [17].

Our simple model of a polymer embedded in a bilayer kept flat by lateral tension has several limitations. For instance, we disregarded the possibility of a backbone elasticity, apart from the stiffness of the polymer constituents. Also, we did not consider configurational fluctuations of the polymers, but assumed them to be uniformly curved. The persistence length was estimated only for a polymer in the straight equilibrium state. Finally, the present theory is restricted to small gradient angles, i.e., to the nearly flat membrane.

There is an analogy between the membrane shape Eq. (2) and the Debye-Hückel theory of the electrical contributions of electrostatic double layers to the bending rigi-

dity for cylindrically bent membranes [18]. The tilt angle of the membrane ridge is related to fields of unequal strength emanating from the two sides of the membrane. In this analogy, J is best taken to correspond to the bulk charge density. However, the Debye-Hückel theory contains no parameter analogous to $\Delta\bar{\kappa}/\kappa$ which is the control parameter in the present case.

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APPENDIX: EFFECTIVE SHAPE OF A RELAXED BILAYER CONTAINING A STRAIGHT CHAIN OF POLYMERIZED MOLECULES

In this section we consider the molecular basis for the rooflike shape of a symmetric surfactant bilayer containing a straight chain of polymerized molecules as introduced in the main part of this work.

We start from the effects of polymerization on a molecular scale. uv irradiation of polymerizable surfactant bilayer produces new chemical bonds between the molecules involved in the polymerization process [1]. This results, as a rule, in changes of the effective molecular shape, in particular, its conic character [19], which we express in terms of a local spontaneous curvature of the bilayer [10]. The effects of possible changes of the bending moduli κ and $\bar{\kappa}$ will be considered only at the end of the Appendix.

We assume that each polymer is restricted to one of the two monolayers. The local spontaneous curvature will depend on where the new chemical bonds are located along the surfactant molecule [1]. A water soluble polymer anchored in the bilayer from one side also produces local bilayer spontaneous curvature if its hydrophobic anchoring groups have an effective shape different from that of the surfactant molecules.

Local spontaneous curvatures modify the shape of the membrane. To analyze this effect we consider an unstressed lipid bilayer which, being symmetric, has zero spontaneous curvature in the unpolymerized state and allows nonzero spontaneous curvature to be induced by polymerization. Let us first consider a hypothetical situation where one of the molecules involved in the polymerization is separated from the polymer chain but keeps the induced spontaneous curvature. If this molecule is embedded into the initially flat unpolymerized bilayer it forms a hat [20]. The top of the hat is formed by the polymerized molecule and has the radius r_{mol} as illustrated in Fig. 5. For simplicity, we assume the hat to be axisymmetric. In the brim of the hat, i.e., for $r > r_{\text{mol}}$, the unstressed membrane has zero total curvature. Accordingly, the cross section of the brim is given by

$$z = z_0 - r_0 \ln[(r/r_0) + \sqrt{(r/r_0)^2 - 1}], \quad (\text{A1})$$

where z_0 is the height and r_0 is the radius of the (imaginary) circle at which the contour of the brim would make the angle $\pi/2$ with the horizontal plane (see Fig. 5).

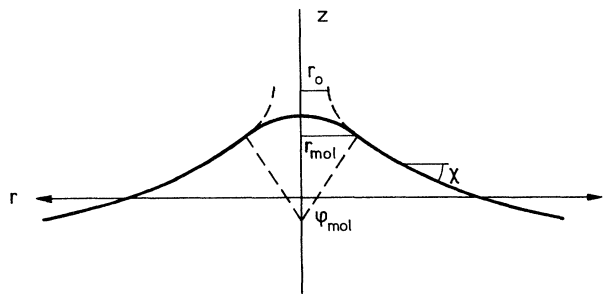


FIG. 5. Schematic cross section of an axisymmetric hat.

We will consider hats with

$$r_{\text{mol}} \gg r_0. \quad (\text{A2})$$

In this case the angle χ made by the contour of the brim with the horizontal plane (Fig. 5) obeys $|\chi| \ll 1$ and can be approximated by

$$\chi = -\frac{dz}{dr} = \frac{r_0}{r}. \quad (\text{A3})$$

It is useful to relate the parameter r_0 of the brim with the characteristics of the polymerized molecule forming the top of the hat. The spontaneous curvature J_{mol} of the polymerized molecule is

$$J_{\text{mol}} = 2\frac{r_0}{r_{\text{mol}}^2}. \quad (\text{A4})$$

The angle φ_{mol} formed by the top of the hat (Fig. 6) is

$$\varphi_{\text{mol}} = 2r_0/r_{\text{mol}}. \quad (\text{A5})$$

We are now in a position to analyze the bilayer shape produced by a straight chain of equal hats as illustrated in Fig. 6. For reasons of simplicity, we assume the hats to be uniformly spaced and the chain to be infinitely long. First we consider a chain where the distance L between the tops of adjacent hats is much larger than the molecular dimension (Fig. 6)

$$L \gg r_{\text{mol}}. \quad (\text{A6})$$

This corresponds to an anchored polymer with large distances between the anchors. The deformation of the membrane by the polymer chain can be obtained by superimposing axisymmetric hats, one for each anchor, as long as the inequality (A2) is satisfied.

In order to find the slope of the membrane as a function of the distance y from the chain [Fig. 6(b)] we calculate the angle χ made by the membrane contour and the horizontal. For $r_{\text{mol}} \gg r_0$, the angle is given by

$$\chi = -\frac{dz}{dy} = -\sum_j \frac{dz_j}{dr_j} \frac{dr_j}{dy}, \quad (\text{A7})$$

where $z_j(r_j)$ is the shape of one hat (A1) and the sum is taken over all hats. For $y \gg L$ the sum can be approximated by an integral replacing the discrete distribution of hats along the x axis by a homogeneous distribution of

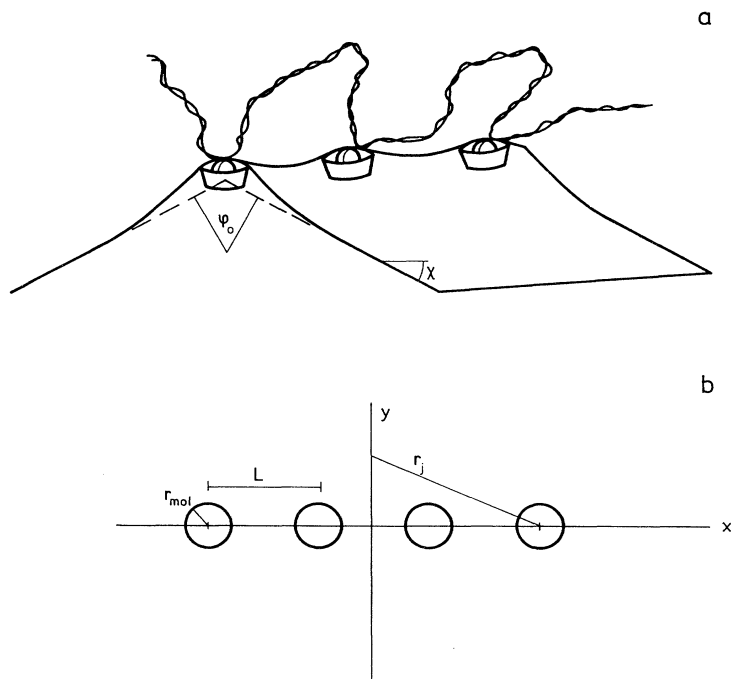


FIG. 6. (a) Shape of a relaxed bilayer containing a straight chain of polymerized molecules. The dashed line illustrates the approximation of the membrane shape by a roof with a sharp ridge. The ridge angle is φ_0 . (b) Schematic projection of the polymer chain on the horizontal plane.

density $1/L$. Because of (A3) and the relationship $r = \sqrt{x^2 + y^2}$ we thus obtain for the angle χ

$$\chi = \sum_i \frac{r_0 y}{x_i^2 + y_i^2} \approx \frac{r_0 y}{L} \int_{-\infty}^{\infty} \frac{dx}{x^2 + y^2} = \pi \frac{r_0}{L}. \quad (\text{A8})$$

The result demonstrates that the slope angle χ at large distances $y \gg L$ does not depend on y . This may have been expected because of the analogy of $z(x, y)$ to the potential of a straight chain of electric charges in two dimensions.

Although the details of the shape of the membrane at small distances from the chain, $y \leq L$, remain to be analyzed, it appears reasonable to approximate the membrane shape on the basis of the result obtained for large distances. The effective shape of the membrane is a roof with a sharp ridge as illustrated on Fig. 6(a) by the dashed line. According to (A8), the angle φ_0 made by the ridge is given by

$$\varphi_0 = 2\pi \frac{r_0}{L}. \quad (\text{A9})$$

Substituting for r_0 from (A4) or (A5) we can relate the ridge angle φ_0 to the spontaneous curvature of a polymerized molecule,

$$\varphi_0 = \pi \frac{r_{\text{mol}}^2}{L} J_s \quad (\text{A10})$$

and to the angle of the top of an isolated hat,

$$\varphi_0 = p \frac{r_{\text{mol}}}{L} \varphi_{\text{mol}}. \quad (\text{A11})$$

Note that the ridge angle φ_0 is much smaller than the angle of an isolated hat φ_{mol} when (A6) applies.

The other shape which we consider is that of an unstressed membrane containing a straight chain of closely packed hats. It corresponds to a water soluble polymer with hydrophobic anchors separated by short distances. In the limiting case of tops in contact with each other this model describes a membrane polymer produced by uv irradiation of polymerizable bilayer.

Using as above the superposition of hats, one can see that the mutual approach of the polymerized molecules in the chain to distances comparable with molecular dimensions, $L \approx r_{\text{mol}}$, changes the shape of each hat. If the top has the shape of a spherical cap at large separations, it assumes a nearly cylindrical curvature as the hats approach each other. This is because each top is exposed to the saddle curvature in the brims of the other hats. Provided the spontaneous curvature, the circular character, and the radius of the hats do not depend on their separation, we obtain for the minimum spacing $L = 2r_{\text{mol}}$ the ridge angle $\varphi_0 = (\pi/2)r_{\text{mol}}J_s$ or $\varphi_0 = (\pi/2)\varphi_{\text{mol}}$ from (A10) and (A11), respectively.

Like the flat membrane, the roof is characterized by a vanishing Gaussian curvature. The same applies to the straight ridge into which a roof is transformed by lateral tension. Being interested mainly in ridges in the stretched and flat membranes, we did not consider any upward or downward bend of the ridge line of the roof. Such a bend is associated with Gaussian curvature.

In this section we have assumed so far the bending moduli κ and $\bar{\kappa}$ to be uniform all over the bilayer. Both of them can actually be different for a polymerized or anchoring molecule in the bilayer. The differences of both moduli produce interactions between the hat tops which may be taken from the recent theory of Goulian, Bruinsma, and Pincus [16] and are assumed to be negligible in the present context.

Interestingly, a difference in $\bar{\kappa}$ will affect the actual local spontaneous curvature. To show this, we write down the bending energy per unit area of a spherically curved hat top

$$\frac{1}{2}(\kappa + \frac{1}{2}\Delta\bar{\kappa})J^2 - \kappa J_{\text{mol}}J,$$

where $\Delta\bar{\kappa}$ is the increase of the modulus of Gaussian curvature in the presence of a polymerized or anchoring molecule in one of the monolayers. ($\Delta\bar{\kappa}$ has to be taken because of the Gauss-Bonnet theorem). Minimization of the last equation yields the actual local spontaneous cur-

vature,

$$J^* = \frac{\kappa}{\kappa + \frac{1}{2}\Delta\bar{\kappa}} J_{\text{mol}}.$$

The result is valid only for $\kappa + \frac{1}{2}\Delta\bar{\kappa} > 0$. Moreover, if $\Delta\bar{\kappa}$ is sufficiently positive, the polymerized molecule will assume saddle curvature instead of spherical curvature. A negative bending energy of the saddle is needed to compensate the positive bending energy of the deformation surrounding the saddle.

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