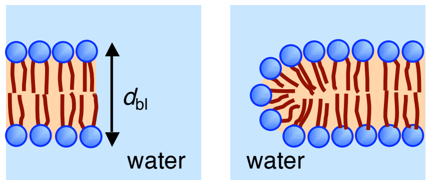
PHYS 4xx Mem 3 - Mechanical instability and failure

When a membrane is stretched under a small tension, its area increases according to the area compression modulus K_A. But if the tension is large enough, the membrane fails at a few percent strain. It's not that that the membrane disintegrates into individual molecules, but rather that a hole forms in it. The boundary of the hole, where it is in contact with the aqueous medium, could be viewed in a couple of way:



(a) (b)

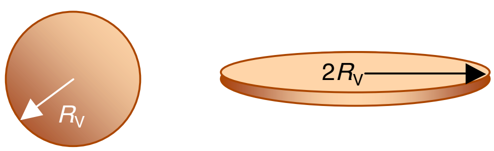
In (a), the hydrocarbon chains are exposed to water, while in (b), the molecular packing defoms to hide the hydrocarbon tails. In either case, there is an energy penalty involved, which we parametrize as an edge tension λ, an energy per unit length, analogous to the surface tension γ. Thus:

$$[\textit{boundary energy}] = \lambda\, [\textit{boundary length}].$$

Note: this is an oversimplification - λ is probably curvature-dependent.

Vesicle formation: *edge energy* vs. *bending energy*

The edge tension λ is what causes a fluid sheet to close up into a vesicle, and it must have a minimum value in order to overcome the bending resistance of the membrane. Consider the two configurations



(a) (b)

The (closed) vesicle shape on the left has a radius R_V. If the sphere and disk have the same area, the radius of the disk must be $2R_V$ according to $4\pi R_V^2 = \pi R_{disk}^2$.

In the simplest curvature model, the energy E_{sphere} required to bend a flat membrane into the shape of a sphere is independent of the sphere radius, and is given by

$$E_{sphere} = 4\pi(2\kappa_b + \kappa_G),$$

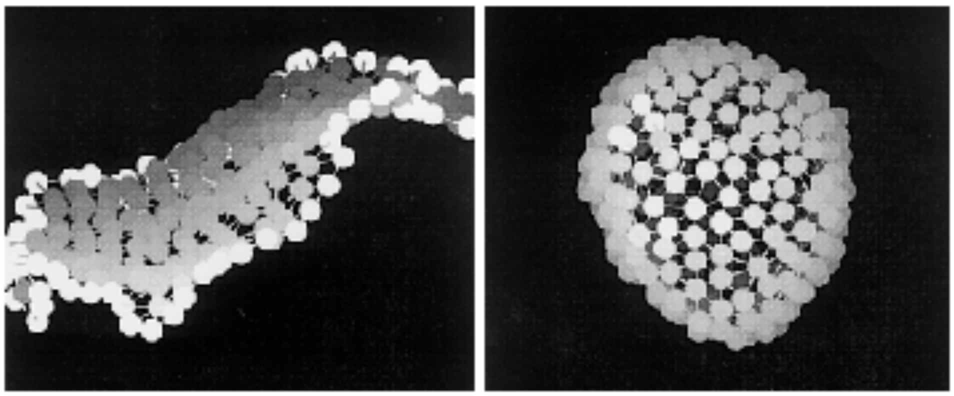
where κ_b and κ_G are the bending rigidities. This energy may be compared to that of a flat disk with a free boundary,

$$E_{disk} = 4\pi R_V \lambda.$$

If R_V is small, $E_{sphere} > E_{disk}$ so that the disk is favored. However, the disk energy increases with perimeter, and the sphere becomes the preferred shape for radii above

$$R_V{}^* = (2\kappa_b + \kappa_G) / \lambda.$$

At non-zero temperature, the curvatures of the surface and the boundary fluctuate locally. Because of their entropy, these shape fluctuations favor the "magic carpet" configuration of the left-hand panel over the handbag in theright-hand panel.



Simulations show that the sheet closes only if λ exceeds a threshold value of

$$\lambda^* = 1.36\ k_B T / b$$

where b is a length scale from the simulation.

Membrane rupture: *edge energy* vs. *tension*

Let's examine the role of edge energy in the failure of a membrane under tension. At T = 0, the system acts to minimize its enthalpy H,

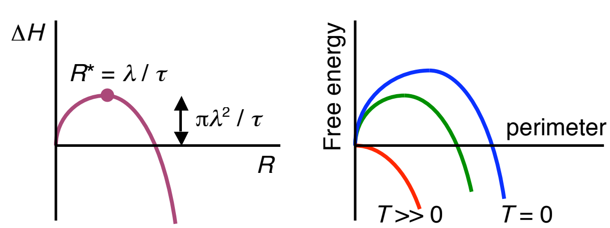
$$H = E - \tau A,$$

where τ is the two-dimensional tension ($\tau > 0$ is tension, $\tau < 0$ is compression).

The energy of a circular hole in the sheet is $E = 2\pi R\lambda$, and the area difference of the sheet + hole system with respect to the intact sheet is just πR^2, where R is the radius of the hole. Hence, ΔH of the membrane + hole system compared to the unbroken membrane is

$$\Delta H = 2\pi R\lambda - \tau \pi R^2.$$

This function is plotted in panel (a):



(a) (b)

The maximum value of ΔH occurs at a hole radius of

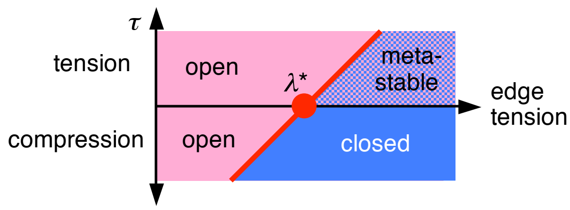
$$R^* = \lambda / \tau.$$

The physical meaning of R^* is that at zero temperature, holes with $R < R^*$ shrink, while those with $R > R^*$ expand without bound.

The effect of temperature ($T > 0$) is to soften the effective edge energy λ, as shown in panel (b) above. The peak in the free energy as a function of perimeter means that there is a barrier between the intact and ruptured states: the intact state is metastable so long as the edge tension is high enough. From simulations, the critical value of the edge tension is

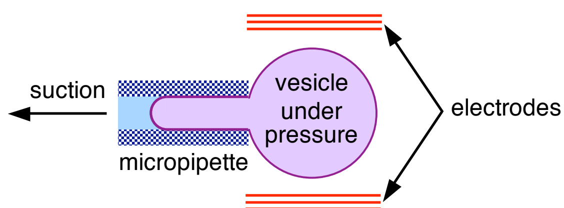
$$\lambda^* = 1.66\ k_B T / b,$$

where b is the mean separation between network points in the simulation. The phase diagram is:



Measured edge tensions

A variety of techniques have been developed over the past 35 years to measure the edge tension. For example, Zhelev and Needham place a pure bilayer vesicle under pressure by aspirating it with a micropipette. Applying an electric field across the vesicle thins the bilayer, creating a hole. The surface stress can be calculated from the aspiration pressure, and the radiius of the hole can be found from the rate of fluid loss.



$\lambda = 0.9 \times 10^{-11}$ J/m for pure stearoyl-oleoyl phosphatidylcholine (SOPC)
$\lambda = 3 \times 10^{-11}$ J/m for SOPC with 50 mol% cholesterol.
$\lambda \sim 0.7 \times 10^{-11}$ J/m for dipalmitoyl phosphatidylcholine (diPPC); Taupin *et al*. (1975).
$\lambda \cong 1.5 \times 10^{-11}$ J/m for DOPC bilayers

Interpretation

If the hole boundary is curved as in the right-hand panel of the first figure, then $\lambda \propto \kappa_b$; this has been confirmed for lipids with n_c = 13 to 22 (Rawicz *et al*, 2000).

Simulations predict $\lambda^* > k_B T/b$, where b is the elementary length scale of the simulation. Taking $b \sim d_{bl} \sim 4 \times 10^{-9}$ m, the simulations predict $\lambda^* > 10^{-12}$ J/m to achieve membrane stability; measured values are about an order of magnitude higher than this, meaning that bilayers are stable against thermal fluctuations.