5. The self-assembly of complex phases

5.1 Phase separation in polymers

Metallurgists make new materials by mixing metals together to make alloys - can we mix up different polymers to make “polymer alloys” with desirable properties? In some cases we can, but it turns out that there are fundamental reasons why it is much more difficult to make new materials from mixing polymers than it is from small molecules.

5.1.1 Flory-Huggins theory of polymer mixtures

Recall that for small molecules we found that the free energy of mixing of a two component mixture could be written, per molecule, as

$$\frac{F_{mix}}{kT} = \phi_a \ln \phi_a + \phi_b \ln \phi_b + \chi\, \phi_a\, \phi_b,$$

where ϕ_A and ϕ_B are the volume fractions of the two components, and χ is a dimensionless interaction parameter, which expresses, in units of kT, the energy change when one takes a molecule of pure A from an environment of pure A and puts it in an environment of pure B. From this free energy we are able to derive the phase diagram, and in particular, we found that the critical value of χ for phase separation had the value 2.

How must this expression be modified to deal with polymers? We consider two polymers, each with degree of polymerisation N.

Recall that the first two terms represent the *entropy of mixing* - this arises from the fact that a single site is either occupied by a molecule of A with probability of ϕ_A, or by a molecule of B with probability of ϕ_B.
If we increase the number of monomer units the molecule from 1 to N, the entropy of mixing *per molecule* stays the same, but the energy of mixing must be increased by a factor of N.

The free energy of mixing per polymer molecule can thus be written

$$\left.\frac{F_{mix}}{kT}\right|_{\text{permolecule}} = \phi_a \ln \phi_a + \phi_b \ln \phi_b + \chi N\, \phi_a\, \phi_b,$$

where χ is the interaction parameter *per segment,* or alternatively we can write the free energy of mixing *per segment* or *per monomer unit* as

$$\left.\frac{F_{mix}}{kT}\right|_{\text{per segment}} = (\phi a/N) \ln \phi a + (\phi b/N) \ln \phi b + \chi\, \phi a\, \phi b.$$

The latter form is more common, and is known as the *Flory-Huggins free energy.*

What are the consequences of this? Once again, the phase diagram can be easily calculated as we did for small molecules. In fact, we can see that all our results for small molecules can be transposed to polymers simply by making the substitution $\chi \rightarrow \chi N$.

In particular, we find that whereas the critical value of χ for phase separation was given by

$\chi_{crit} = 2$ small molecules

for polymers we have

$\chi_{crit} = 2/N$.

Don't forget that N can be anything up to 10,000 or more.

Even a very slightly unfavourable interaction causes polymers to phase separate.

Why is this? The reason is in the *entropy of mixing.* Small molecule mixtures can have an unfavourable energetic interaction, but still mix, because their entropy of mixing overcomes the unfavourable energetic interaction.

But polymers are much bigger molecules, and their entropy of mixing is correspondingly smaller.

Most polymers do not mix.

If we do try to mix polymers, we get phase separated mixtures, usually with very poor mechanical properties. This is why it is so difficult to recycle plastics.

5.1.2 Phase separation mechanisms

Polymers phase separate by the same mechanisms as small molecule mixtures, that is by *nucleation and growth* or by *spinodal decomposition,* according to what part of the phase diagram one quenches them into.

The theory of spinodal decomposition for polymers is essentially the same as that for small molecules, discussed in section 2.4. The only variation comes mathematically in the precise form of the gradient coefficient, and physically in how this is interpreted.

Recall that the theory of spinodal decomposition starts from the observation that there is a free energy cost of maintaining a sharp concentration gradient. We wrote the free energy as

$$F = A \int \left(f_0(\phi) + \kappa \left(\frac{\partial \phi}{\partial x} \right)^2 \right) dx,$$

where κ is the *gradient energy coefficient.*

For polymers, the gradient energy coefficient takes the form (at the critical composition)

$\kappa = Na^2/9.$

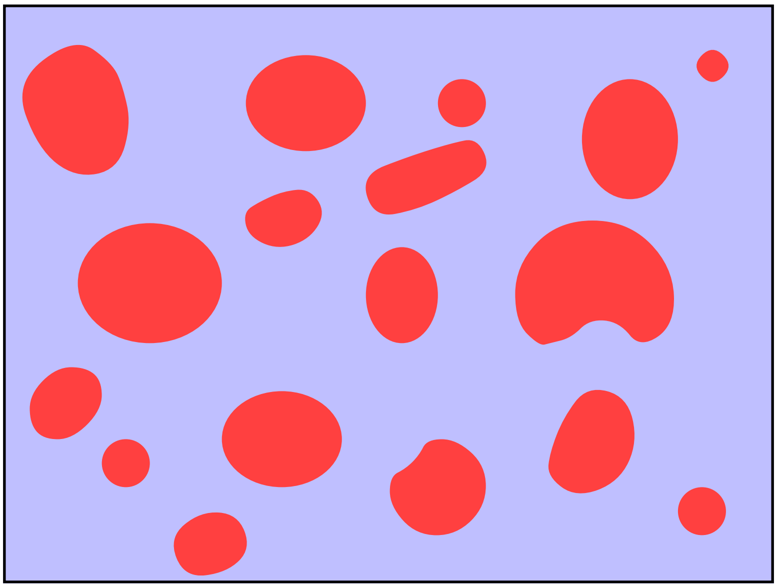
where we write the free energy *per molecule,* (rather than per segment we did for the Flory-Huggins free energy).

Note that Na^2 is simply the mean squared end-to-end distance of the chain.

The interpretation of this is that it starts to cost free energy whenever the concentration gradient becomes steep compared to the overall size of the chain. This is because to create such large concentration gradients, the chain has to be in a lower entropy configuration than an unperturbed random walk.

5.1.3 The interface between immiscible polymers

Given that most polymer pairs will not mix, the structure that one will ultimately obtain will consist of domains of one polymer dispersed in a matrix of the other polymer.

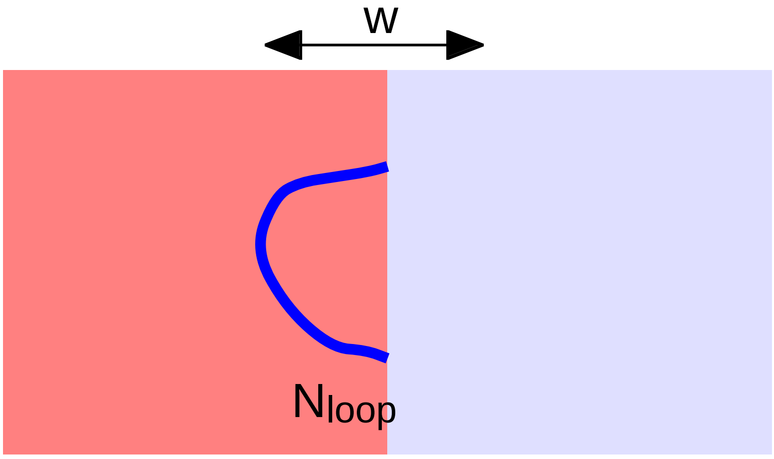


What is the nature of the interface between the two different polymers?

We should not expect it to be atomically sharp, because the polymers are random walks, and this would reduce their configurational entropy too much. Instead, we expect to get some interpenetration of the polymer chains across the interface.

Schematic diagram of a polymer-polymer interface, showing partial interpenetration of chains on either side of the interface.

We can use our knowledge of random walks to estimate both the width of the interface and the interfacial energy.



Suppose the interface is characterised by a width w.

On average, we will have loops of one chain of length N_{loop} penetrating into the the foreign material on the other side of the interface.

The loop will be itself a random walk, so we can write

$w \sim a \sqrt{N_{loop}}$.

Associated with the loop will be an unfavourable energy coming from the N_{loop} contacts between A and B segments;

interaction energy $\sim \chi N_{loop}\, kT$.

But at equilibrium this interaction energy will be about kT, so

$1 \sim \chi N_{loop}$.

Substituting for N_{loop} in terms of w we find an estimate for the interfacial width

$w \sim a/\sqrt{\chi}$.

Typically this is of order 1 - 3 nm. The distance betwen entanglements is 5 - 10 nm, so although there is interpenetration at polymer/polymer interfaces it is not sufficient for the polymers to become entangled. This is why most mixtures of polymers are weak, and it is difficult to glue plastics together.

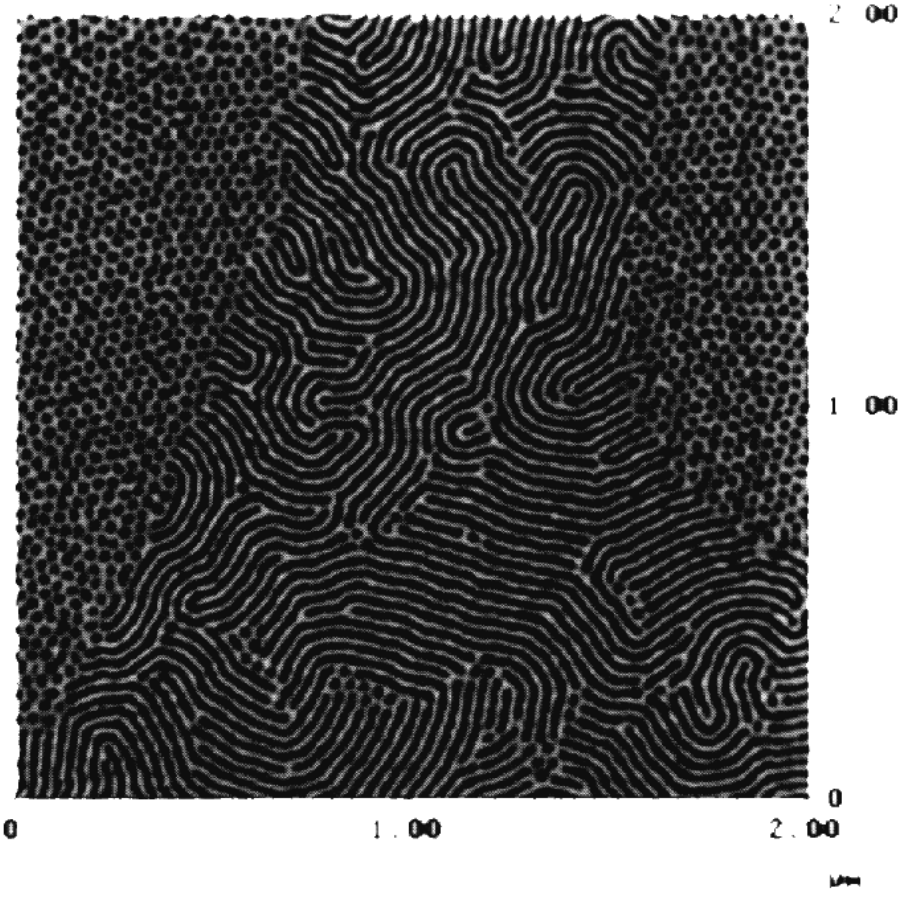
We can also estimate the interfacial energy γ by counting the number of unfavourable contacts per unit area, each of which has an energy χkT:

$$\gamma \sim \frac{kT}{a^2}\sqrt{\chi}.$$

It turns out that although the argument leading to these two results is very crude, much more sophisticated theories essentially confirm them.

5.2 Microphase separation in block copolymers

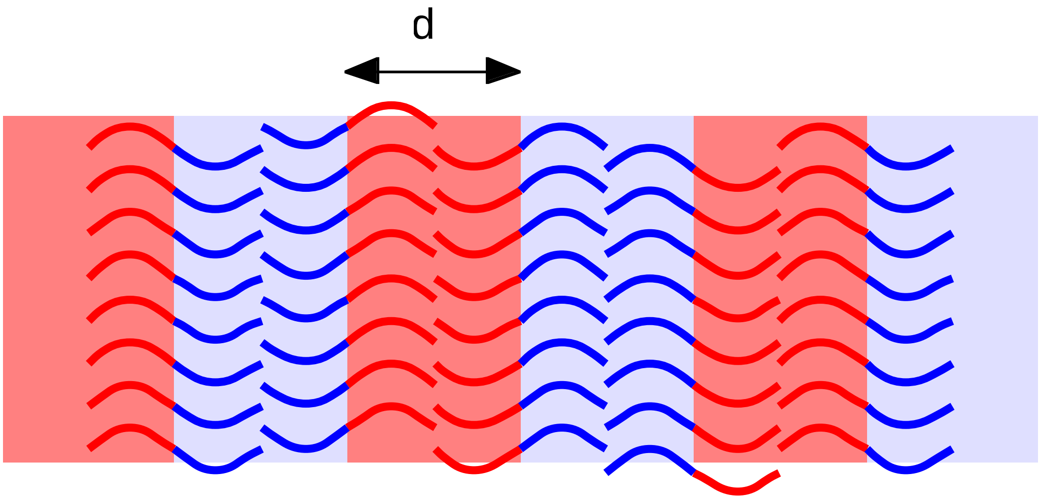
As we saw in section 3, block copolymers consist of two lengths of chemically different polymers joined together covalently. If the interaction between the two blocks is unfavourable, the two chemical species would like to phase separate, but the covalent bond between them frustrates their tendency to phase separate macroscopically. The result is that phase separation is restricted to a microscopic scale, with complex morphologies determined by a delicate balance of energy contributions. An example is shown below.



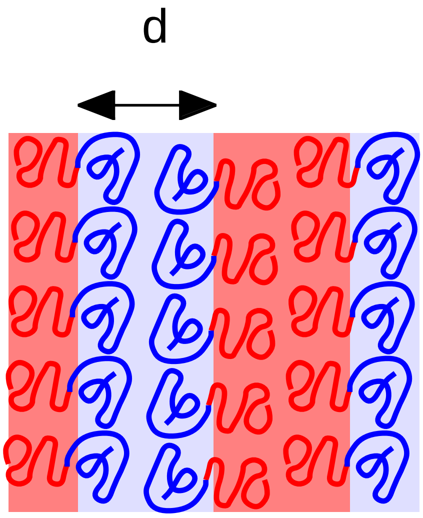
The surface of a commercial triblock copolymer of styrene and butadiene (Kraton D-1102), as revealed by atomic force microscopy (van Dijk and van den Berg).

5.2.1 Microphase separation versus macro-phase separation

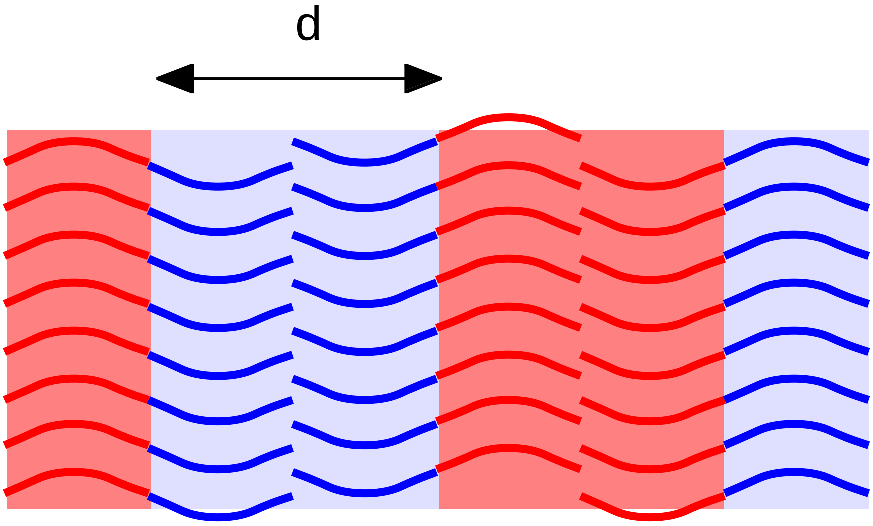
The basic physics of microphase separation is best illustrated by considering a diblock copolymer each of whose blocks is of identical molecular weight. Here the balance between the tendency of the two halves of the copolymer to segregate and their constraint leads to a *lamellar* morphology - a regular alternation of layers of each of the two chemical species.



The thickness of the lamellae, d, is extremely regular and well-defined. What determines its value? Once again, it is given by a balance of free energies. The larger d is, the less area of interface there is per unit volume, and thus the lower the interfacial energy. On the other hand, in order to fit into thick lamellae, the chains have to stretch out to longer than their random walk sizes and this reduces their entropy.



d small - chains are close to random walk configuration, but there is a large amount of interfacial energy.



d large - less interface, but the chains are now strongly stretched.

We can estimate the equilibrium lamellar spacing by writing down the total free energy as a sum of the stretching contributions and the interface contribution and finding d to minimise this.

The free energy due to chain stretching per chain can be written as

$\frac{d^2}{Na^2}kT$; per unit volume we have a total of $1/Na^3$ chains.

Per unit volume the amount of interface we have is 1/d, so the total interfacial energy is γ/d.

The total free energy F(d) per unit volume then is

$$F(d) \sim \frac{\gamma}{d} + \frac{1}{Na^3}\frac{d^2}{Na^2}kT \quad .$$

Minimising this with respect to the lamellar spacing d we find

$$d \sim \left(\frac{\gamma\, a^5}{kT}\right)^{1/3} N^{2/3}.$$

If we use the expression we derived above in section 5.1.3 for the interfacial tension between immiscible polymers,

$$\gamma \sim \frac{\mathrm{kT}}{\mathrm{a}^2}\sqrt{\chi},$$

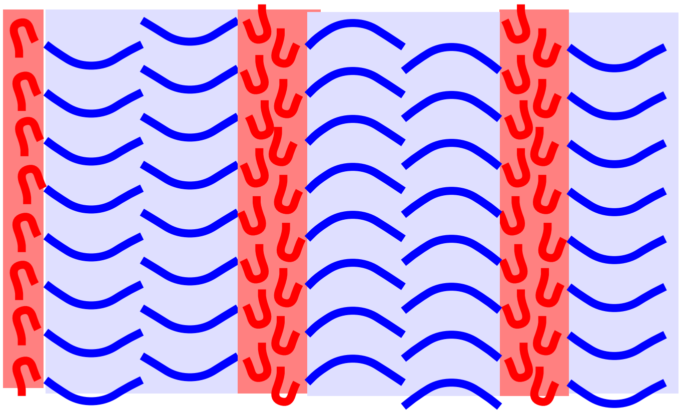
we find

$$d \sim a\chi^{1/6} N^{2/3}.$$

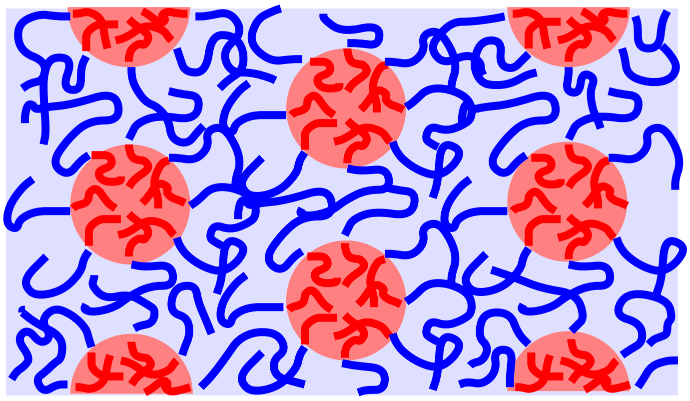
This expression is valid in the limit $\chi N >> 1$.

5.2.2 The phase diagram for block copolymers

If the two blocks of a diblock are not of equal length, then the lamellar morphology is less favourable, because the shorter blocks end up less stretched than the long ones. This leads to a tendency for the interface to become curved.

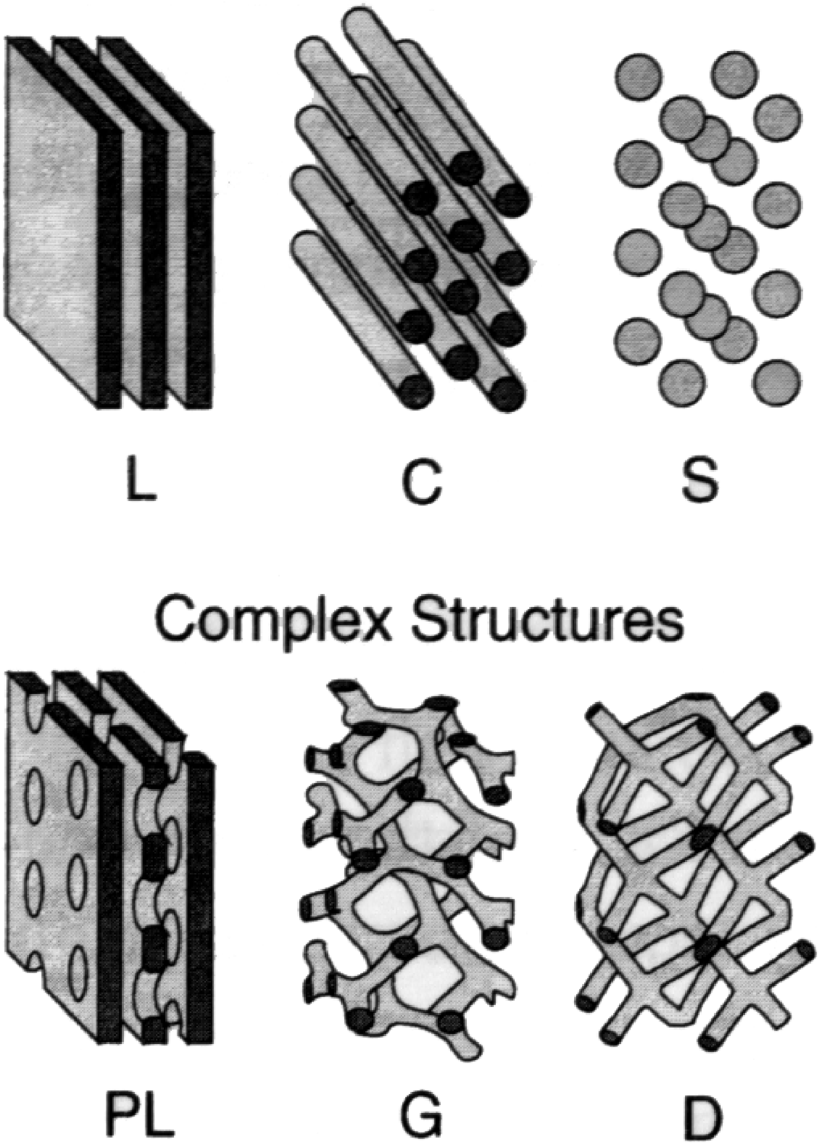


A lamellar morphology for a diblock with one block shorter than the other. The long blocks are more stretched than the short blocks, with the effect that there is a tendency for the interfaces to become curved:



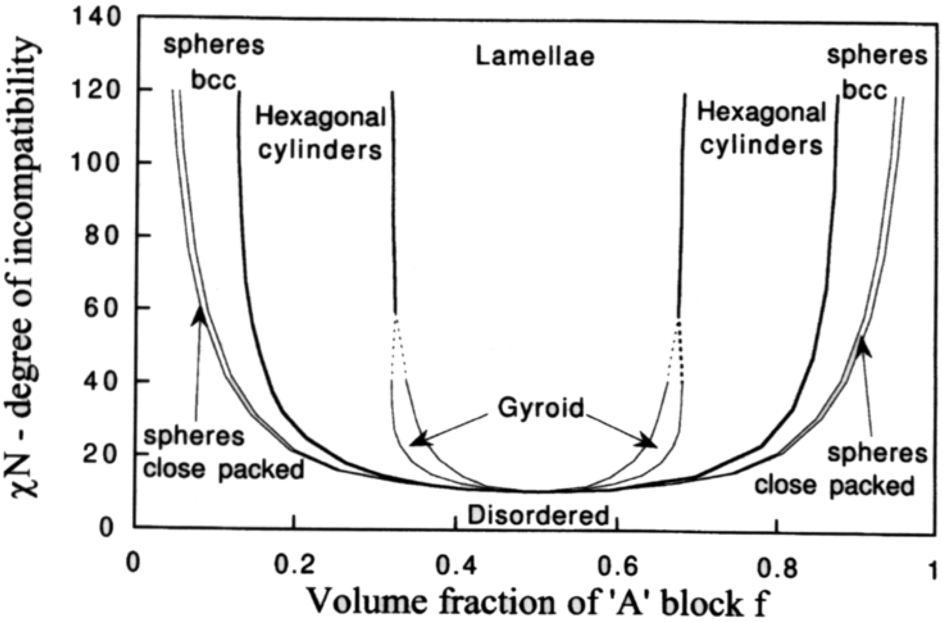
Thus as we change the ratio between the block lengths in block copolymers we will change the equilibrium morphologies.

For strongly immiscible blocks, the morphology changes from lamellar to hexagonally packed cylinders with increasing asymmetry, then it changes to spheres, packed firstly in a body-centred cubic array, then in a close packed array (the difference in energies between hexagonal close packed and face centred cubic is probably indetectable practically). In addition, more complicated structures have been observed.



Block copolymer morphologies. L, C and S (Lamellae, cylinders and spheres, respectively are the so-called classical morphologies which have been known for about 20 years. PL, G, and D (perforated lamellae, gyroid and double diamond) were first observed more recently.

The phase diagram can be predicted, using theories that are too sophisticated to discuss here. The simplest case is for diblocks with in which block has an identical length.



The phase diagram for a symmetrical diblock polymer, as calculated by self-consistent field theory (Matsen and Bates).

Note that on the axis of the diagram is the product of the Flory-Huggins interaction parameter χ and the degree of polymerisation N. Note that the value of χN needed to obtain microphase separation is more than 10, in contrast to the value of 2 needed for a polymer mixture to phase separate.

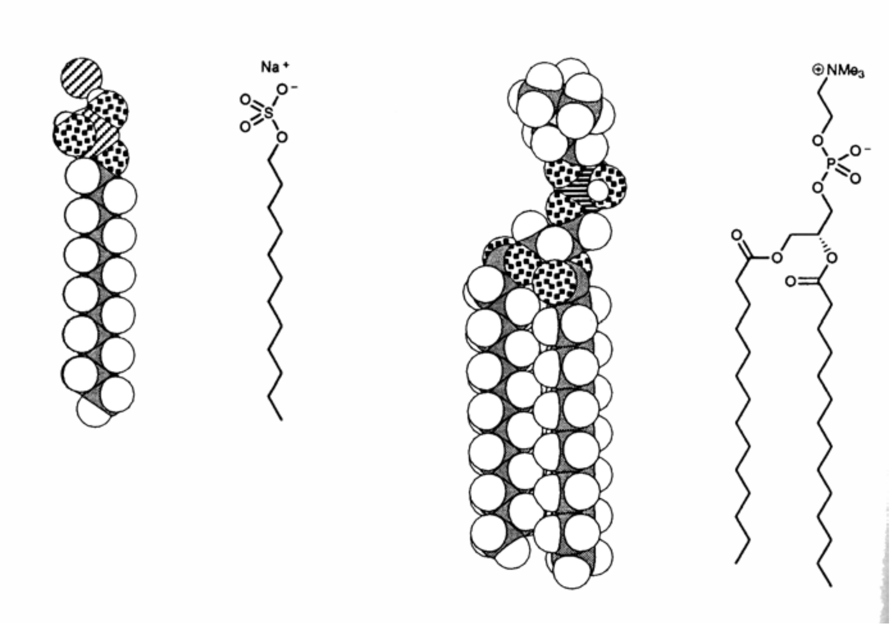
This phase diagram predicts a window of stability for the gyroid phase, but the other complex phases, perforated lamellae and the bicontinous double diamond, although they have been experimentally observed, have not been accounted for theoretically. It is possible that they are not equilibrium phases at all, but are phases that are kinetically trapped because the kinetics of transforming into the equilibrium structure are too slow to be observable.

5.3 Complex phases in amphihile solutions

An amphiphile is a molecule which has one end that has a favourable interaction with water (i.e. is *hydrophilic)* and one end that has a favourable interaction with oils or hydrocarbons (i.e. it is *hydrophobic).* This ambivalence between oil and water usually results in a tendency for such molecules to segregate to surfaces and interfaces.

Usually the hydrophobic part of the molecule is a hydrocarbon chain with about 12-20 carbon atoms. The hydrophilic part may be charged or uncharged. Examples of surfactant are given below:

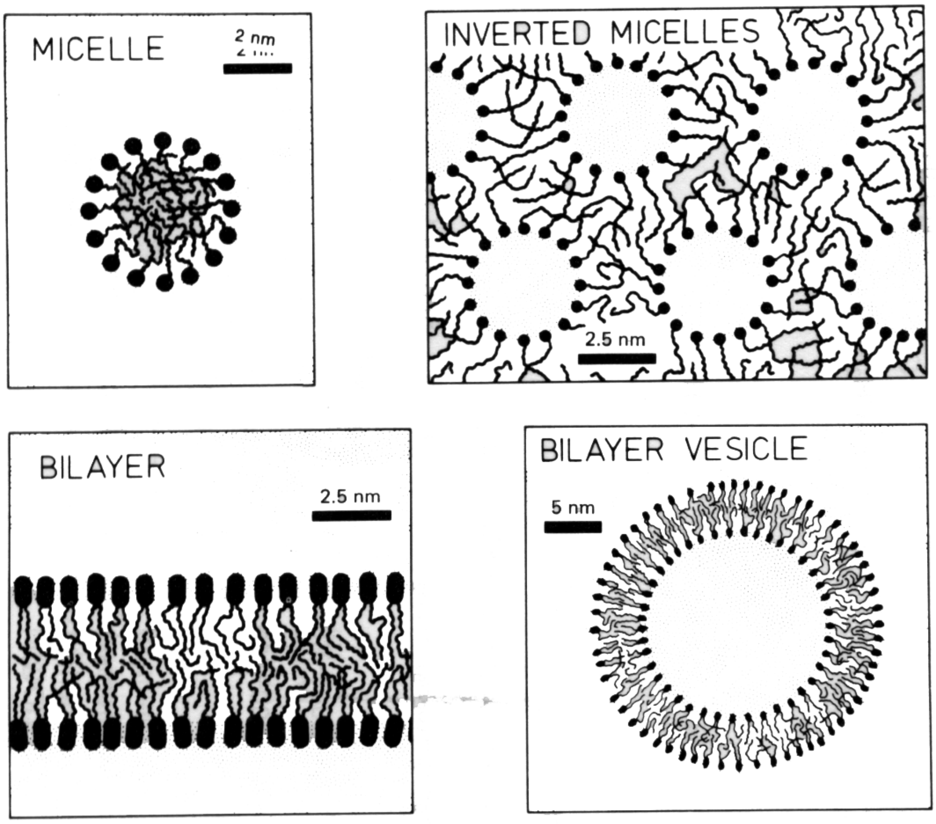
Example	hydrophobic group	hydrophilic group	category	where found
Sodium stearate	$C_{18}H_{37}$	$-COO^-$ Na^+	Anionic	Soap
Sodium dodecyl sulphonate	$C_{12}H_{25}$	$-O-SO_3^-$ Na^+	Anionic	Detergents
Hexadecyl trimethylammonium bromide (CTAB)	$C_{16}H_{33}$	$-N^+ (CH_3)_3$ Br^-	Cationic	Mild disinfectants
$C_{12}E_5$	$C_{12}H_{25}$	$-(-O-CH_2CH_2)_5$	Non-ionic	Cosmetics
Lecithin	Two chains, each $C_{12}H_{25}$	phosphatadyl choline	Zwitterionic, Phospholipid	Animal membranes, food



Amphiphilic molecules. On the left is sodium dodecyl sulphonate, a typical synthetic detergent whose structure is very similar to soap. On the right is diphosphatidyl choline, a phospholipid which is a major component of cell membranes as well as being the main ingredient of the food emulsifier lecithin.

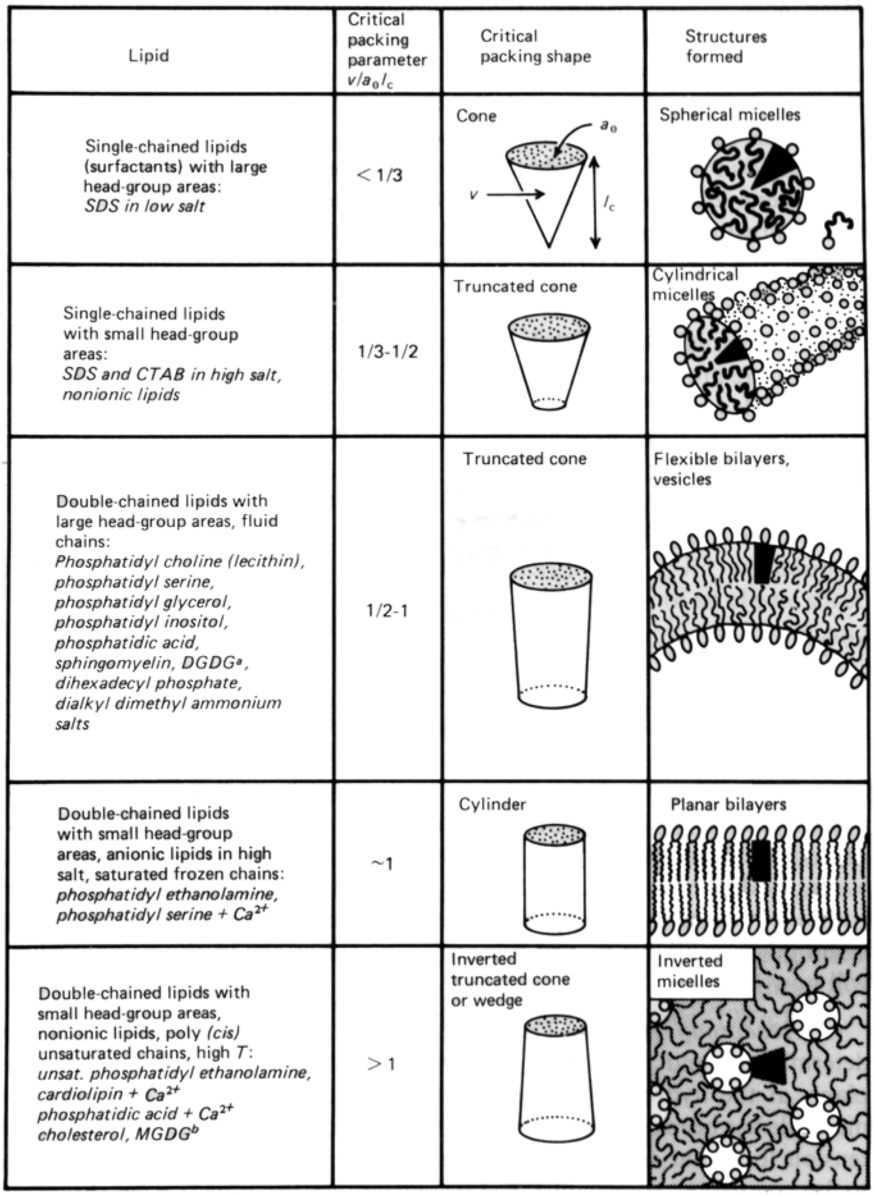
5.3.1 Self assembly of amphihile solutions and the effect of curvature

When dissolved in water, amphiphiles *self-assemble* in such a way that their hydrophobic tails are kept together away from the water. The most common unit into which self-assembly takes place is the spherical micelle, though other shapes are also possible.



Self-assembled structures in surfactant solutions. From Israelachvili.

What determines the shape of the self-assembled structure in a surfactant solution? The single most important factor is the *packing shape* of the surfactant, and the resulting natural curvature of the interface between water and the self-assembled structure.



Lipid	Critical packing parameter $v/a_0 l_c$	Critical packing shape	Structures formed
Single-chained lipids (surfactants) with large head-group areas: *SDS in low salt*	$< 1/3$	Cone	Spherical micelles
Single-chained lipids with small head-group areas: *SDS and CTAB in high salt, nonionic lipids*	1/3-1/2	Truncated cone	Cylindrical micelles
Double-chained lipids with large head-group areas, fluid chains: *Phosphatidyl choline (lecithin), phosphatidyl serine, phosphatidyl glycerol, phosphatidyl inositol, phosphatidic acid, sphingomyelin, DGDG*[a]*, dihexadecyl phosphate, dialkyl dimethyl ammonium salts*	1/2-1	Truncated cone	Flexible bilayers, vesicles
Double-chained lipids with small head-group areas, anionic lipids in high salt, saturated frozen chains: *phosphatidyl ethanolamine, phosphatidyl serine +* Ca^{2+}	~1	Cylinder	Planar bilayers
Double-chained lipids with small head-group areas, nonionic lipids, poly *(cis)* unsaturated chains, high *T*: *unsat. phosphatidyl ethanolamine, cardiolipin +* Ca^{2+} *phosphatidic acid +* Ca^{2+} *cholesterol, MGDG*[b]	> 1	Inverted truncated cone or wedge	Inverted micelles

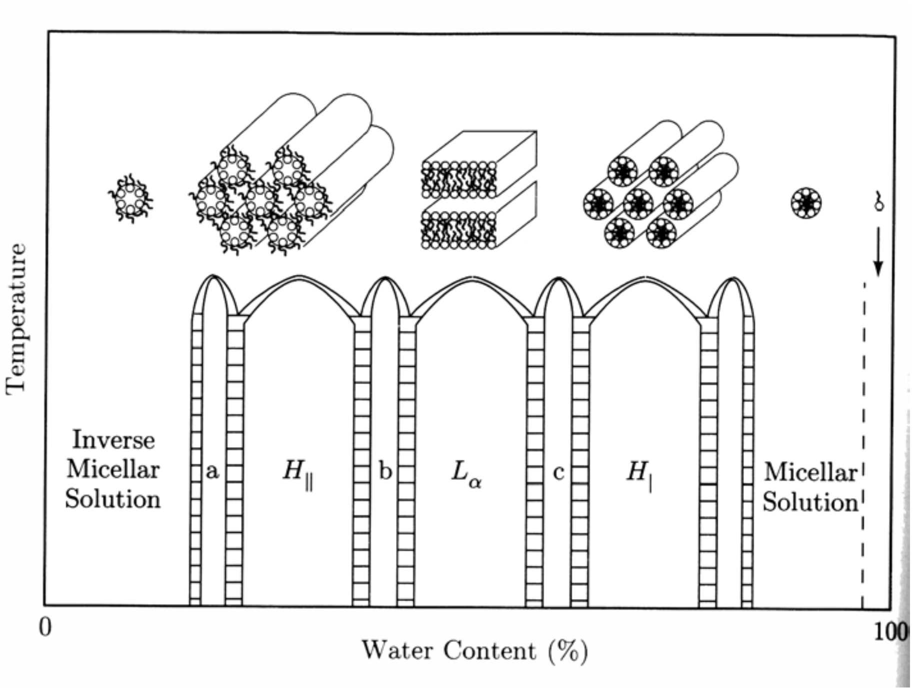
[a] DGDG, digalactosyl diglyceride, diglucosyl diglyceride.
[b] MGDG, monogalactosyl diglyceride, monoglucosyl diglyceride.

Packing shapes of various surfactants, and the structures they form. From Israelachvili.

5.3.2 Complex phases and microemulsions

The simple structures formed by self-assembled amphiphiles are spheres, cylinders and lamellae, or sheets. These basic units can themselves be arranged in supramolecular structures which can have a high degree of order.

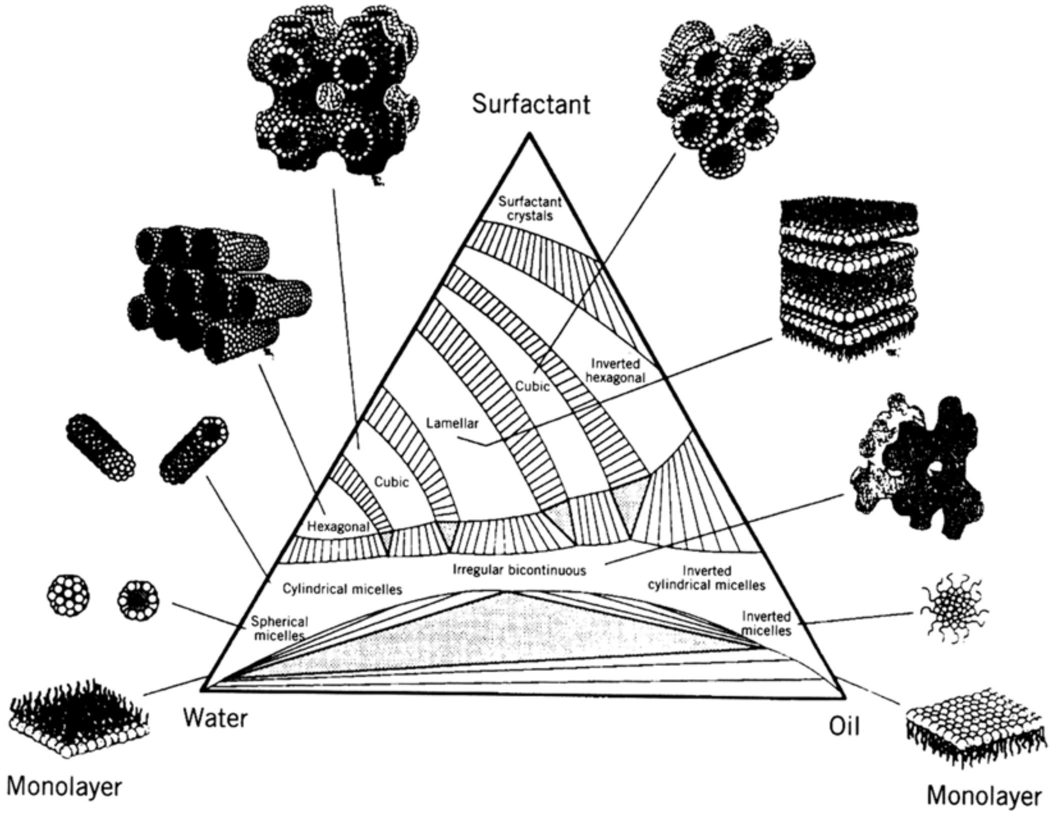
In a simple mixture of an amphiphile and water, an example of the sort of phase diagram one obtains is shown below:



Schematic phase diagram for mixtures of an amphiphile and water, showing the structure of the micellar and liquid crystalline phases.

Note that the ordered phases H_I, H_{II}, and L_α are *mesophases* with liquid crystalline order.

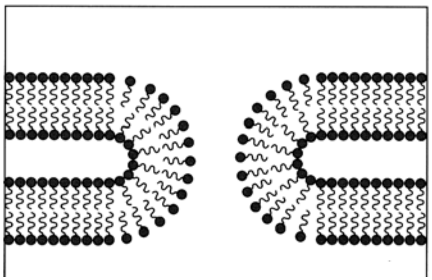
Another dimension of complexity is added when one adds as a third component to the mixture an oil. Essentially, at low concentrations the oil molecules swell the amphiphile micelles. At higher concentrations of oils their are some new kinds of phases, and other phases which are sometimes present in the simple water/amphiphile mixtures become more prominent.



Schematic phase diagram of an oil/water/amphiphile mixture.

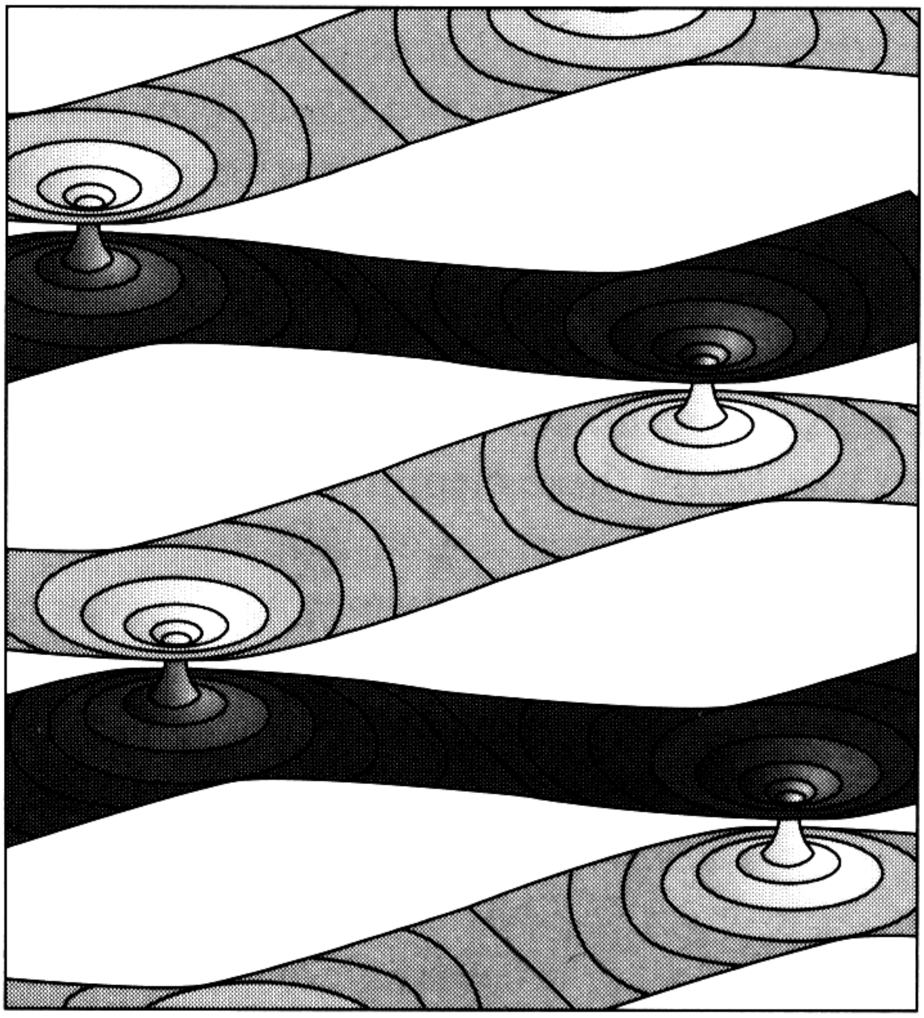
A feature of these more complex phase diagrams is the appearance of more complex phases, such as the irregular bicontinuous (or *sponge*) phase, and the cubic phases. The latter actually have full three dimensional order, and as such are essentially supramolecular solids, with a non-zero shear modulus.

One can see how these new phases arise by considering lamellae. Two adjacent sheets in the lamellae can form a pore, shown below. This costs energy as it involves a sharp distortion in the shape of the sheets, but introduction of these pores creates *entropy* .



A pore connecting two lamellar sheets.

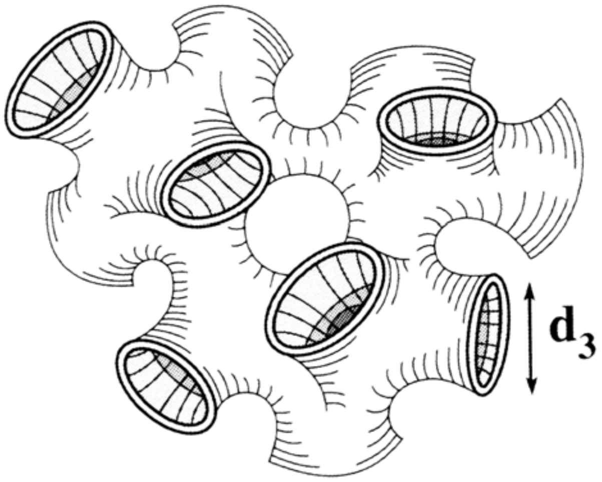
In some circumstances the entropic contribution to the free energy outweighs the energy penalty of having the pores, and one has an equilibrium phase of randomly perforated lamellae.



A perforated lamellar phase.

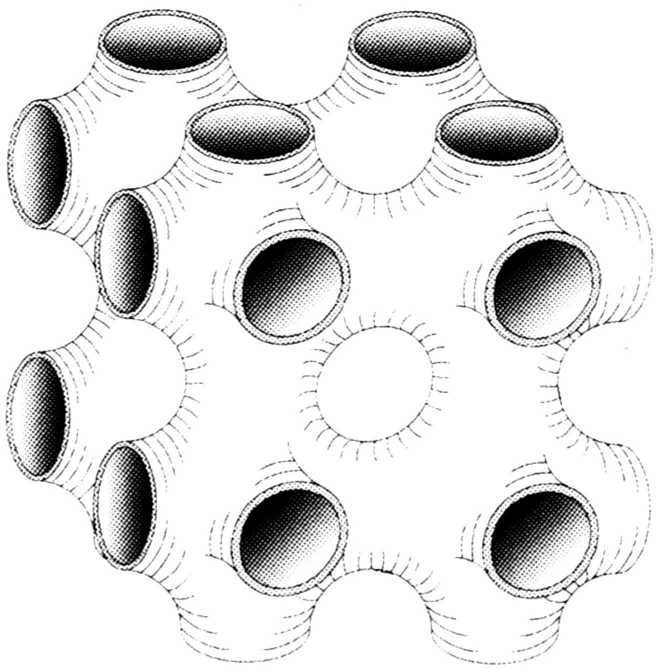
Note that this perforated lamellar phase divides space up into two separately interconnected regions.

A structure which is topologically equivalent to the perforated lamellar structure, but which is fully disordered, is called a *sponge phase,* or sometimes, more colourfully, a *plumber's nightmare.*



The sponge phase, or plumber's nightmare. The characteristic length scale of the tubes, d_3*, is of the same order as the interlamellar spacing in a lamellar phase.*

Much more regular analogues of the sponge phase are also possible, in which the interconnected tubes are arranged on a regular lattice. One such structure is the cubic P phase. The structure of this are shown below.

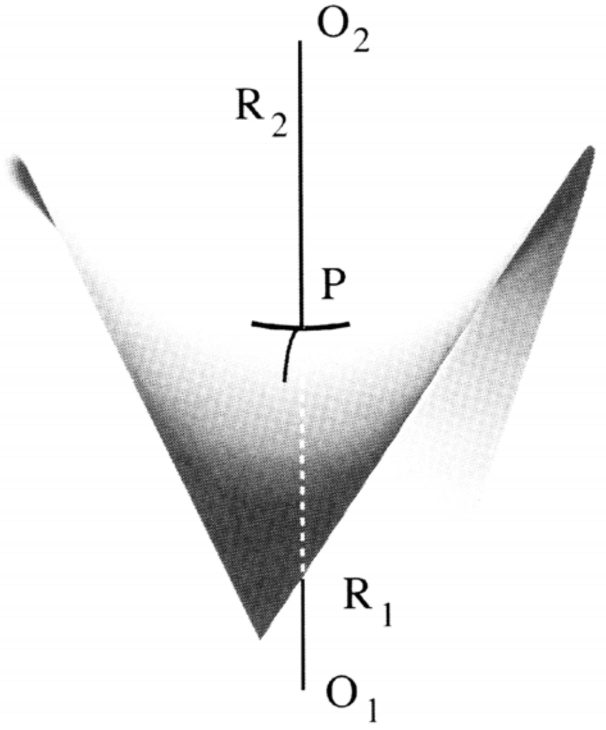


The cubic P phase.

How can we characterise such complex structures? Once again, a key quantity is *curvature*. A bilayer membrane, from which such structures are composed, must have the same pressure on either side to be at equilibrium. Recall that the pressure difference near a curved interface is given by the equation

$$\Delta P = \gamma \left(1/r_1 + 1/r_2 \right)$$

where r_1 and r_2 are the radii of curvature in two perpendicular directions. ($1/r_1 + 1/r_2$) is referred to as the mean curvature. The cubic P phase is made up of saddle shaped units which have a zero mean curvature, ensuring that there is no difference in pressure on either side of the bilayer.



Saddle deformation. The principal curvature radii at point P, R_1 and R_2, are equal in magnitude but opposite in sign. The mean curvature is therefore zero.

The cubic P phase is just one of a number of possible periodic structures in which a membrane is arranged in a way in which the mean curvature is zero.