

Chapter 5

Surfactants

5.1 Surfactant phases

Surfactants are molecules constructed in such a way that one end (called “hydrophilic”) prefers water or aqueous mixtures, and the other end (called “hydrophobic”) prefers nonpolar, hydrocarbon solvents. Such molecules, which can be of biological or artificial origin, are strongly attracted to the interfaces between otherwise immiscible solvents.

Surfactants serve several useful functions. They can reduce the interfacial tension between oil and water, promoting the wetting of hydrophobic surfaces by water (or hydrophilic surfaces by oil), which is how soaps work to promote the removal of insoluble dirt and oil. Surfactants can be used to prepare emulsions of water in oil or vice versa; mayonnaise, chocolate mousse and many other sauces are prepared in this way. Emulsions can be used to suspend otherwise insoluble solutes in aqueous solution; modern water-based coatings, pesticides, and many other products are prepared in this way.

Surfactants typically have either one or two short (C_6 – C_{20}) hydrocarbon tails, joined to a polar headgroup. The headgroup can be one of several types: 1) nonionic, made typically of a short piece of polyethylene oxide; 2) cationic, consisting of a positive ionic group (typically quaternary ammonium) and a dissociating anion (typically bromine or chlorine); 3) anionic, consisting of a negative ionic group (typically sulfonate or carboxylate), and a dissociating cation (typically sodium); 4) zwitterionic, consisting of a strong dipole that does not dissociate in water.

In those cases in which the surfactant headgroup becomes charged by dissociation of its counterion, the behavior of the resulting micelles or other structures is strongly affected by Coulomb interactions. We defer the discussion of such phenomena until later lectures, and focus here on the behavior of nonionic surfactants.

A variety of phases can be formed by surfactants in combination with two immiscible solvents. Some of the structures are strongly analogous to copolymer micellar phases we have discussed in previous lectures. Indeed, there is a strong analogy between surfactants and diblock copolymers, which may be described as “polymeric surfactants”. Like diblocks, surfactants in a single solvent can form spherical and cylindrical micelles as well as bilayer vesicles. Some surfactants can form micelles in either oil or water; in oil we speak of “inverted micelles” (as water is presumed to be the more common choice of solvent).

In the presence of two immiscible solvents (generically “oil” and “water”), the possibilities are multiplied. “Swollen micelles” can be formed, in which the core of the micelle is expanded to incorporate a volume of the solvent compatible with the micellar core. Finally, more exotic phases can be formed, of which two are of particular note: 1) bicontinuous microemulsions, in which the

geometry is a randomly interpenetrating network of connected oil and water regions separated by surfactant monolayers, with a typical length scale for the “thickness” of the regions (distance to the nearest opposite phase) of several hundred Angstroms; and 2) “sponge” phases, which have a geometry like that of bicontinuous microemulsions, except that the surfactant monolayers are replaced by bilayers, and *both* sides of the bilayer are the *same* phase (either oil, or water).

Bending expansion

Our treatment of the competition among different self-assembled micelles and microphases of diblock copolymers was based on the competition between unfavorable contacts between monomers (or for the micelles, between the core blocks and the nonsolvent outside), and the entropy reduction implied by the stretching of chains in the assemblage. For surfactants, we do not have a comparable microscopic description of the free energy of surfactant structures. Instead, we take advantage of the disparity in thickness of the surfactant layer (of order 10 Angstroms) and the typical thickness of swollen micelles, emulsion droplets, or microemulsion structures that we shall consider here (of order 100–1000 Angstroms).

For such problems, the surfactant layer is a thin sheet, the free energy of which can be regarded as a function of its shape, and of the area density of surfactants. Typically, the system can adjust the area per surfactant, in order to minimize the total free energy. We expect that the area per surfactant is approximately constant, as the surfactant layers are in some sense a two-dimensional fluid, with cohesive energy and hard-core repulsive interactions, leading to an approximately incompressible behavior.

For example, consider a system forming swollen micelles, in which both the total quantity of surfactant and interior phase are fixed. The system can adjust to accommodate both these constraints by adjusting the radius of the micelles, be they spherical or cylindrical. In extreme cases, when there is far too much interior solvent, the system may reject some of the interior solvent to form an additional demixed phase. When there is far too little solvent, the system may likewise reject some of the surfactant to form micelles.

What remains to determine the free energy of a surfactant layer is then its shape. Locally, a portion of interface is characterized by its radii of curvature. Every small region of a surface near some given point P can be fit to a small portion of a paraboloid, which takes the form

$$h(\xi, \eta) = (1/2) ((\kappa_1 \xi)^2 + (\kappa_2 \eta)^2) \quad (5.1.1)$$

in an appropriately chosen local coordinate system (in which P is taken as the origin, the orthogonal ξ and η axes lie within the tangent plane, and are oriented to be lined up with the principal curvature directions of the local bit of surface).

The principal curvatures at P are κ_1 and κ_2 . They have units of inverse length, and are the reciprocals of the radii of curvature of the surface along the two principal curvature directions, denoted R_1 and R_2 . A way to visualize the curvature radii is to imagine a circle fitted to the surface, residing in the plane defined by one of the principal curvature directions ($\hat{\xi}$ or $\hat{\eta}$) and the surface normal \hat{n} .

The mean and Gaussian curvatures H and K are defined in terms of the κ_i as

$$\begin{aligned} H &= (1/2)(\kappa_1 + \kappa_2) \\ K &= \kappa_1 \kappa_2 \end{aligned} \quad (5.1.2)$$

The free energy per unit area f can be expanded in powers of these curvatures, which are small if the layer is nearly flat; i.e., if the curvatures are small compared to the layer thickness. Then we

may expand f in a Taylor series to second order in the curvatures κ_1 and κ_2 ,

$$f = f_0 + f_1(\kappa_1 + \kappa_2) + f_2(\kappa_1^2 + \kappa_2^2) + f_3\kappa_1\kappa_2 + \dots \quad (5.1.3)$$

in which we have imposed the symmetry requirement that f be invariant under exchange of κ_1 and κ_2 .

Rearranging slightly and renaming the coefficients gives

$$F/\text{area} = 2k(H - c_0)^2 + \bar{k}K \quad (5.1.4)$$

in which c_0 is the spontaneous curvature, k is the bending modulus, and \bar{k} the Gaussian modulus.

The total free energy of the interface is then simply the area integral of the above,

$$F = \int dA (2k(H - c_0)^2 + \bar{k}K) \quad (5.1.5)$$

Now it turns out there is an amazing theorem in the mathematics of surfaces, the Gauss-Bonnet theorem, which states that the area integral of the Gaussian curvature over a closed surface is a topological invariant — independent of the detailed shape of the surface, depending only on the number of “handles” of the surface.

The result is

$$\int dA K = 4\pi(1 - g) \quad (5.1.6)$$

in which g is the “genus” of the surface, informally the “number of handles” — zero for a sphere, one for a torus, and so forth. For present purposes, the point of the Gauss-Bonnet theorem is that the Gaussian curvature term is a topological constant. A negative Gaussian modulus \bar{k} favors spheres over cylinders and lamellae; a positive value favors shapes with lots of “handles” — “foamy” structures like microemulsions, for example.

The physics of curved interfaces is relatively simple, but the math can be a bit messy. One result we will have need of later is an expression for the layer normal \hat{n} in terms of the layer shape. Formally, the layer normal is a unit vector orthogonal to any pair of vectors tangent to the surface. If we regard the surface locally as “parameterized” (depending on) two variables u and v , we may write

$$\hat{n} = \frac{\partial_u \vec{r} \times \partial_v \vec{r}}{|\partial_u \vec{r} \times \partial_v \vec{r}|} \quad (5.1.7)$$

This approach can be used to calculate the normal.

A somewhat simpler way is to define a “level function” F , which is zero on the surface:

$$0 = F(x, y, z) = z - h(x, y) \quad (5.1.8)$$

This relation by itself does not define $F(x, y, z)$ off the surface; we can extend the definition near to the surface, so that a small perpendicular distance dh away, $F = dh$. Now the gradient of F is perpendicular to the surface, because F is constant on surface. Hence the normal \hat{n} is proportional to ∇F , which we can compute explicitly as

$$\hat{n} = \frac{\nabla F}{|\nabla F|} = \frac{\hat{z} - \nabla h}{\sqrt{1 + (\nabla h)^2}} \quad (5.1.9)$$

Finally, it turns out to be useful to relate mean curvature to $\nabla \cdot \hat{n}$. (We do not usually need an expression for the local Gaussian curvature, because of the Gauss-Bonnet theorem.) In the coordinate system defined by local tangents (for example, the principal curvature axes), we know

\hat{n} only varies in surface, not along its own length. That is, \hat{n} may be regarded as locally constant along its own direction, $(\hat{n} \cdot \nabla)\hat{n} = 0$. Whereas, the variation of \hat{n} along the curvature directions can be seen geometrically to giving us the two principal curvatures. So we have

$$H = \nabla \cdot \hat{n} = -\nabla \cdot \left(\frac{\nabla h}{\sqrt{1 + (\nabla h)^2}} \right) \quad (5.1.10)$$

which gives us an explicit formula for the mean curvature of a layer described by a height function $h(x, y)$.

Emulsification and its limits

Suppose we add a small amount of surfactant to a two-phase system of water plus some oil. At first, the surfactant will be consumed in the production of a small number of spherical swollen micelles, of the optimal curvature, dispersed in water. Such a phase is called a droplet microemulsion. The optimal structure is computed by minimizing the bending free energy with respect to the curvatures,

$$0 = 2k((\kappa_1 + \kappa_2)/2 - c_0) - |\bar{k}|\kappa_2 \quad (5.1.11)$$

and similarly for κ_1 exchanged with κ_2 . This implies $\kappa_1 = \kappa_2 = \kappa$, which leads to

$$\kappa^* = \frac{2kc_0}{2k + \bar{k}} \quad (5.1.12)$$

As more surfactant is added, more droplets are produced until one of two things happen; 1) the droplets become crowded in the water, or 2) we run out of oil to fill the droplets. Here, we focus on the second possibility, that the droplets become starved for oil. To accommodate the added surfactant, the system can make the droplets smaller (which uses the surfactant “less efficiently”, as it were, consuming less oil to fill the droplets). Eventually, the droplet radius will be far from the optimal value. Alternatively, the system can produce a phase that by its geometry is less efficient in covering a given volume of oil — namely, either cylinders or lamellar layers.

To find out which structure coexisting combination of structures leads to the lowest bending energy, Turkevich and coworkers compared the bending energies of spheres, cylinders, and lamellae subject to the geometrical constraints imposed by given amounts of surfactant and oil. Those constraints take the form

$$\begin{aligned} nA\delta &= \phi_s \\ nV &= \phi_o \\ V/A &= \phi_o\delta/\phi_s \end{aligned} \quad (5.1.13)$$

in which there are n micelles of area A and volume V , a volume fraction ϕ_s of surfactant, and a volume fraction ϕ_o of oil in the system.

The result of their calculations is an emulsification phase diagram, presented as a function of two variables r and x . The variable $x = -\bar{k}/(k + \bar{k}/2)$ is a measure of the Gaussian curvature that emerges from the analysis; for larger values of x , spheres are preferred because of the Gaussian curvature term that favors multiple closed objects of genus zero (no handles). The variable $r = 3\kappa^*\delta\phi_s/\phi_o$ is a dimensionless ratio of the sphere radius required to accommodate all the surfactant and all the oil (namely $3\delta\phi_s/\phi_o$) over the optimal radius $1/\kappa^*$.

The resulting phase diagram shows that when r exceeds unity — which means that if all the oil were to be incorporated in droplets, their radius would exceed the optimal size — the system

responds by rejecting the excess oil; this is called “emulsification failure”. If we starve the system of oil, spheres begin to coexist with cylinders, unless the Gaussian modulus is sufficiently negative to favor spheres over cylinders. If we starve the system sufficiently, what little oil there is can be used to line the space between flat bilayers to produce a lamellar phase in which all the surfactant can be incorporated.

(The calculation does not consider the possibility that surfactant in the starved case would instead form a coexisting phase of spheres at the optimal size and micelles; nor does it, in its simplest form, take account of the relatively minor effects of translational entropy of the spheres or cylinders.)

5.2 Fluctuations of interfaces

In addition to the well-ordered phases described in the previous lecture, surfactants also exhibit phases with more complicated structures, including phases in which random organization of surfactant monolayers or bilayers is an essential element of the phase stability.

Consider a “balanced” surfactant, designed so that its spontaneous curvature at an oil-water interface vanishes. Suppose we introduce this surfactant in increasing concentrations into an initial 50-50 mixture of oil and water. Before the surfactant is added, the oil and water will be phase separated, with a macroscopic regions of oil and water — ideally, a single region of oil atop a single region of water, with a planar interface between. The first surfactant added will go predominately to the oil-water interface; some may dissolve singly in the oil or water, but these concentrations will be small if the surfactant is “strong”, i.e., has large unfavorable interactions of its two halves with the “wrong” liquid. Some of the surfactants added may also form spherical micelles to gain translational entropy, but these are disfavored for a balanced surfactant.

Once the preexisting interface is saturated, where will additional surfactant go? Because it is balanced, one may argue it prefers largely flat interfaces; so one possibility is to form a lamellar phase, of alternating layers of oil and water separated by surfactant monolayers. But if the bending stiffness of the surfactant monolayer is not too large (of order kT , say), something more interesting results; namely, a bicontinuous microemulsion, in which randomly connected oil and water regions are separated by monolayers, with a typical length scale ξ for the “thickness” of the regions (distance from within an oil region to the nearest water region, say) of a few hundred Angstroms. “Bicontinuous” means that both the oil and water regions are connected in all directions.

Microemulsions are entropically stabilized: the cost of deforming the monolayers away from strictly planar interfaces turns out to be compensated by the increased configurational entropy of the randomly connected structure. (The above arguments assume an interface without significant Coulomb interactions, resulting from either a nonionic (neutral) surfactant, or ample salt in the water phase to “screen” the interactions of charged surfactants.)

If we add surfactant that forms a microemulsion to an oil-water mixture, then, the surfactant is accommodated by incorporating the required amounts of oil and water to use up the surfactant in forming microemulsion. The microemulsion, with a density intermediate between oil and water, sits between the oil and water in an equilibrated vessel; such microemulsions are consequently known as “middle-phase” microemulsions. In contrast, surfactants with nonzero spontaneous curvature when added to oil-water mixtures will be accommodated by forming droplet microemulsions, either oil droplets dispersed in the water phase (a “lower-phase” microemulsion) or water droplets dispersed in the oil phase (an “upper-phase” microemulsion).

Another exotic possibility is to consider a surfactant interface in which the Gaussian stiffness is positive, therefore favoring geometries with large numbers of “handles”. In such a case, various three-dimensional periodically bicontinuous structures form, called “plumber’s nightmare” (PN) phases because of the infinite network of “pipes” and “joints” they contain. These phases can form in the presence of oil and water, or just with one liquid, which case can be envisioned as a PN phase with the oil sucked out, draining the “interior” liquid from within the phase until a three-dimensional periodic micellar network remains.

It turns out that surfactants can also form other exotic phases in a single liquid (oil, say), in which one would expect the local structure to be a bilayer. Evidently, balanced surfactants in a single liquid could form lamellar phases (stacks of bilayers separated by oil), or bilayer vesicles (closed “bags” of oil surrounded by bilayer, floating in excess oil). But also, such bilayers can form analogs of the microemulsion phases, in which we replace the water regions with oil, and replace the surfactant monolayers with bilayers. Thus we have the possibility of “sponge” phases analogous

to bicontinuous microemulsions, in which two randomly connected oil regions are separated by a surfactant bilayer.

Our description of microemulsions left unanswered the question of what determines the length scale ξ . It turns out that surfactant interfaces, like polymers, have a persistence length, on which scale they bend spontaneously as a result of thermal fluctuations. In the next section, we develop a description of fluctuations in planar surfactant interfaces, in order to understand how entropy can stabilize microemulsions, as well as to investigate the role of entropy in surfactant lamellar phases.

Fluctuations of surfactant interfaces

In our discussion of spherical, cylindrical, and lamellar domains formed from surfactant monolayers, we took full advantage of the uniform curvature in those idealized geometries. To investigate fluctuations in planar interfaces, we must deal with an interface of varying shape and curvature.

We start with the bending energy,

$$E = \int dA (1/2)kH^2 \approx \int d^2x (1/2)k(\nabla^2 h)^2 \quad (5.2.1)$$

Here we have expanded the mean curvature to lowest order in the height function $h(x, y)$ describing the location of the interface (surfactant monolayer or bilayer) in terms of its height above the x - y plane. We have also dispensed with the Gaussian curvature term, since it integrates to a constant as long as the interface remains planar in topology.

It is useful to represent the energy in terms of Fourier modes of the surface $h(q)$, because the energy is “diagonal” in terms of these modes, i.e., each mode makes an independent, quadratic contribution to the energy.

$$E = \int \frac{d^2q}{(2\pi)^2} (1/2)kq^4 |h(q)|^2 = \frac{1}{A} \sum_q (1/2)kq^4 |h(q)|^2 \quad (5.2.2)$$

In the second equality we have converted from an integral to a sum, by taking $dq = 2\pi/L$ as appropriate for large system with periodic boundary conditions. We can absorb the factor of $1/A$ with a redefinition

$$h_q = h(q)/A^{1/2} \quad (5.2.3)$$

For reference, the relation between the original height function and its transform is

$$h(r) = \int \frac{d^2q}{(2\pi)^2} e^{iq \cdot r} h(q) = \frac{1}{A^{1/2}} \sum_q e^{iq \cdot r} h(q) = \sum_q e^{iq \cdot r} h_q \quad (5.2.4)$$

The partition function can be written in terms of a sum over the amplitudes of the interface modes, as

$$Z = \sum_{\text{mode ampls}} e^{-\beta E} = \prod_q \int dh_q e^{-\beta(1/2)kq^4 |h_q|^2} \quad (5.2.5)$$

With the partition function, we can evaluate averages over fluctuating mode amplitudes, or the free energy itself, using techniques from previous lectures.

The integrals over the complex mode amplitudes are slightly tricky. First of all, h_q is complex, so the integral $\int dh_q$ is really a two-dimensional integral, over the real and imaginary parts $\Re(h_q)$ and $\Im(h_q)$. Also, we remember that for $h(r)$ to be real, we must have $h_{-q} = h_q^*$. So for every

wavevector q , we can pair together the positive and negative q terms (which have the same energy), so that the contribution to the energy for a given q and $-q$ is

$$\beta dE = \beta k q^4 (\Re(h_q)^2 + \Im(h_q)^2) \quad (5.2.6)$$

Then we interpret $\int dh_q$ as a two-dimensional integral $\int d\Re(h_q) d\Im(h_q)$.

Then, using Gaussian integral results, we can evaluate after some algebra

$$\langle |h_q|^2 \rangle = \langle \Re(h_q)^2 + \Im(h_q)^2 \rangle = \frac{1}{\beta k q^4} \quad (5.2.7)$$

Height and tangent fluctuations.

Now we can evaluate the mean-square displacement of points on a surface due to fluctuations, with

$$\begin{aligned} \langle h^2(r) \rangle &= (1/A) \sum_{q, q'} e^{iq \cdot r} e^{iq' \cdot r} \langle h_q h_{q'} \rangle \\ &= \frac{T}{kA} \sum_q \frac{1}{q^4} \\ &= \frac{T}{k} \int \frac{d^2q}{(2\pi)^2} \frac{1}{q^4} \\ &= \frac{T}{2\pi k} \int_{2\pi/L}^{\infty} q dq q^{-4} \sim \frac{TL^2}{k} \end{aligned} \quad (5.2.8)$$

We see that the height fluctuations grow with the size L^2 of the patch of interface, and are proportional to the ratio T/k , so that stiffer interfaces have smaller fluctuations.

By similar means we can evaluate the correlation function for the layer normal,

$$g(r) = \langle (\hat{n}(r) - \hat{n}(0))^2 \rangle \quad (5.2.9)$$

When r is small, $\hat{n}(r)$ and $\hat{n}(0)$ point in nearly the same direction, and $g(r)$ is near zero. As r increases, the normals at distant points become uncorrelated, and $g(r)$ grows to be about two. Using the expression $\hat{n} = (\hat{z} - \nabla h) / \sqrt{1 + (\nabla h)^2}$, we have

$$\begin{aligned} g(r) &= 2(1 - \langle \hat{n}(r) \cdot \hat{n}(0) \rangle) \\ &\approx 2(\langle (\nabla h(0))^2 \rangle - \langle \nabla h(r) \cdot \nabla h(0) \rangle) \end{aligned} \quad (5.2.10)$$

Now $\langle (\nabla h(0))^2 \rangle$ is a dimensionless constant, so to get an idea of how $g(r)$ grows we focus on the first term. We substitute for $h(r)$ in terms of its Fourier transform, convert from $h(q)$ to h_q , to obtain

$$\delta g(r) = 2 \langle \nabla h(r) \cdot \nabla h(0) \rangle = \frac{2}{A} \sum_q q^2 e^{iq \cdot r} \langle |h_q|^2 \rangle \quad (5.2.11)$$

Now use our earlier result for the average $\langle |h_q|^2 \rangle$, and the fact that the integral is even in q , to write

$$\delta g(r) = \frac{T}{kA} \sum_q q^{-2} \cos(q \cdot r) \quad (5.2.12)$$

Convert back to an integral,

$$\begin{aligned} \delta g(r) &= \frac{T}{k} \int \frac{d^2q}{(2\pi)^2} q^{-2} \cos(q \cdot r) \\ &= \frac{T}{2\pi k} \int q dq q^{-2} J_0(qr) \end{aligned} \quad (5.2.13)$$

This is a slightly nasty integral to evaluate for large r (which is the limit we want). Our efforts are aided by taking the derivative with respect to r , making use of $J_0'(r) = -J_1(r)$, so that

$$\begin{aligned} g'(r) &= -\frac{T}{2\pi k} \int dq J_1(qr) \\ &= -\frac{T}{2\pi kr} \int_0^\infty dx J_1(x) \\ &= \frac{T}{2\pi kr} J_0(x)|_0^\infty = -\frac{T}{2\pi kr} \end{aligned} \tag{5.2.14}$$

We can now integrate this result to find the behavior of $g(r)$ itself, as

$$g(r) = T/(2\pi k) \log r/a \tag{5.2.15}$$

in which we have imposed a microscopic cutoff at which $g(r)$ has the value zero expected for small r .

When $g(r)$ is of order unity, the normals are uncorrelated; this occurs at a characteristic length scale $\xi \sim a \exp(\beta k/2\pi)$. If the membrane is floppy (k is of order kT), this “persistence length” for the membrane is small; for stiff membranes, ξ is exponentially large. We may expect that on the length scale ξ , bending the membrane will be relatively cost-free, because bends on this length scale occur spontaneously.

This result suggests the basic strategy for designing surfactants to form microemulsions should include a requirement that the bending stiffness not be too large (not more than a few kT). This means intuitively that the surfactants cannot be too long (else the interface would be thick, and more difficult to bend). On the other hand, for the surfactant to be strongly attracted to the oil-water interface, the tails must be long enough and the headgroup hydrophilic enough that the energy of isolated surfactants in either phase is large. Thus we expect a relatively narrow range of molecular weights for good microemulsion-forming surfactants, which is in fact found to be true.

5.3 Fluctuating lamellar phases

In the last lecture, we considered the effect of fluctuations on a single planar interface controlled by a bending stiffness, for which we computed the persistence length, as defined by the tangent correlation function. We also calculated the mean-square fluctuation of the vertical position of such a membrane, and found that $\langle h^2 \rangle$ grew with the linear dimension L as TL^2/k .

Now consider a lamellar phase of such membranes, with average spacing d between adjacent layers. Thermal fluctuations will lead to collisions between layers. Since the layers cannot cross each other, the confinement of the membranes to a stack will reduce the entropy of the layers, relative to the entropy of an isolated membrane.

We may expect that this reduction in entropy of layers in a stack will lead to an entropic repulsion between the layers, or equivalently an entropically generated compressional modulus for a lamellar phase of fluctuating layers. This entropically generated repulsion between undulating layers controlled by bending stiffness is called a Helfrich repulsion.

Scaling argument for Helfrich repulsion

We can formulate a scaling argument for the magnitude of the Helfrich repulsion, how it depends on the bending stiffness k and the layer spacing d , as follows. We estimate the typical volume per collision in the stack, and assert that the entropic cost per collision will be of order kT on the grounds that to avoid the collision, we can adjust the amplitude or phase of a single mode of one of the colliding layers.

We estimate the volume per collision by finding the area of a patch of interface such that the mean-square height fluctuation of a single layer is of order d . We showed earlier that the mean-square height fluctuation $\langle h^2 \rangle$ of an isolated layer of linear dimension L scales as TL^2/k . Equating this to d^2 , we find the “area per collision” scales as

$$L^2 \sim kd^2/T \quad (5.3.1)$$

Hence the free energy per unit volume from entropy loss due to collisions would scale as

$$F/V \sim T^2/kd^3 \quad (5.3.2)$$

To find the corresponding compressional modulus, suppose we change the spacing of the stack of layers slightly. We define the compressional modulus as

$$B = d^2 \frac{\partial^2 f}{\partial d^2} \quad (5.3.3)$$

in which $f = F/V_0$ is the free energy per layer per unit area (V_0 is the unperturbed volume of the system, not touched by the derivative).

This is consistent with the usual definition of isotropic compressional modulus of a liquid as $KV = V^2 \partial^2 F / \partial V^2$, or equivalently $K = v \partial^2 F / N \partial v^2$ where $v = V/N$ is the volume per molecule (N the number of molecules). We can see this by writing analogously $BV = h^2 \partial^2 F / \partial h^2$ in which $h = nd$ is the height of the entire system and n is the (fixed) number of layers, which leads immediately to the above equation for B .

Applying this expression for B to the scaling result for the free energy of a lamellar stack, we find that B scales in the same way as F/V , namely as T^2/kd^3 .

Self-consistent calculation of B

Now we present a more systematic calculation of B , beyond a scaling theory. The calculation is self-consistent, in the following sense: the fluctuations of layers in a stack are reduced by the influence of the very compressional modulus we are trying to calculate. So we calculate the free energy of a stack of interacting layers, assuming an interlayer interaction of an unknown strength; we then impose that the compressional modulus computed from the resulting free energy is the same as the one assumed in computing the free energy in the first place.

Our starting point is the energy per unit area for a stack of membranes, each with bending stiffness, and each interacting with adjacent membranes in the stack via an effective repulsive interaction:

$$E/\text{area} = b/2 \sum_n (h_n - h_{n-1})^2 + k/2 \sum_n (\nabla_{\perp}^2 h)^2 \quad (5.3.4)$$

in which h_n is the height of the n th layer above some reference plane, b is the effective interlayer repulsive interaction, and k the bending stiffness of the layers.

Taking the continuum limit, we have an energy functional

$$E = \int d^3x \left((1/2)B (\partial_z h)^2 + (1/2)K (\nabla_{\text{pert}}^2 h)^2 \right) \quad (5.3.5)$$

in which we have defined $B = bd$ and $K = k/d$, where d is the mean spacing between adjacent layers, and $h(r) = h(z, x)$ is the vertical displacement of a layer with nominal height z and in-plane position x .

We convert this energy expression into a more tractable form for performing averages, by rewriting it in terms of Fourier modes of h :

$$\begin{aligned} E &= (1/2) \int \frac{d^3q}{(2\pi)^3} (Bq_z^2 + Kq_{\perp}^4) |h(q)|^2 \\ &= 1/(2V) \sum_q (Bq_z^2 + Kq_{\perp}^4) |h(q)|^2 \\ &= 1/V \sum_q (Bq_z^2 + Kq_{\perp}^4) |h_q|^2 \end{aligned} \quad (5.3.6)$$

In the above, we have used the same relations between $h(q)$ and $h(r)$, between Fourier integrals and sums over wavevectors, and between $h(q)$ and h_q , as were introduced in the discussion of fluctuations of a single interface. In three dimensions, these read

$$\begin{aligned} h(q) &= \int d^3x e^{-iq \cdot r} h(r) \\ dq &\approx 2\pi/L \\ h_q &= h(q)/V^{1/2} \end{aligned} \quad (5.3.7)$$

That is, the integral over q can be regarded as a sum over a finely spaced grid of points with spacing $2\pi/L$ in each direction, for a system of linear dimension L with periodic boundary conditions, and we define h_q by convention to absorb the resulting factor of $1/V$ where $V = L^3$.

Now we can write the partition function for the system of fluctuating, interacting layers as

$$Z = e^{-\beta F} = \prod_q \int dh_q e^{-\beta/2(Bq_z^2 + Kq_{\perp}^4)|h_q|^2} \quad (5.3.8)$$

This expression is simple because the sum over each mode amplitude h_q is an independent Gaussian integral, which simplicity results from the energy being the sum of independent, quadratic contributions from each mode.

The only details to be careful about are 1) the modes h_q are actually complex numbers,

$$h_q = \Re h_q + i\Im h_q \quad (5.3.9)$$

and 2) the mode amplitudes for q and $-q$ are related according to

$$h_{-q} = h_q^* \quad (5.3.10)$$

because $h(q)$ is the Fourier transform of a real-valued function. So for each pair of wavevectors q and $-q$ we can consider the integrals over $x_q = \Re h_q$ and $y_q = \Im h_q$ together,

$$Z = \prod_q' \int dx_q \int dy_q e^{-\beta(Bq_z^2 + Kq_\perp^4)(x_q^2 + y_q^2)} \quad (5.3.11)$$

in which the prime on the product indicates that we have taken only half of the wavevectors, those that have $q_z > 0$ for example.

With this expression, we can compute the free energy itself, as well as the mean-square amplitude of the q th mode, $\langle |h_q|^2 \rangle$. For the mode amplitude, we note that

$$\begin{aligned} \langle |h_q|^2 \rangle &= \langle x_q^2 + y_q^2 \rangle \\ &= 2\langle x_q^2 \rangle \\ &= \beta(Bq_z^2 + Kq_\perp^4) \end{aligned} \quad (5.3.12)$$

in which the last result follows from the ‘‘equipartition theorem’’ (which is to say, from the result for Gaussian integrals of the form $\int dx x^2 e^{-\alpha x^2}$ divided by the normalization $\int dx e^{-\alpha x^2}$).

For the free energy, we have

$$\begin{aligned} \beta F &= -2 \sum_q' \log (Bq_z^2 + Kq_\perp^4)^{-1/2} + \text{const} \\ &= (1/2) \sum_q \log (Bq_z^2 + Kq_\perp^4) + \text{const} \end{aligned} \quad (5.3.13)$$

This we convert back to an integral,

$$\beta F/V = (1/2) \int \frac{d^3 q}{(2\pi)^3} \log (Bq_z^2 + Kq_\perp^4) \quad (5.3.14)$$

(in which we have silently dropped the constant).

Correspondingly, the difference in free energy between layers in a stack at mean spacing d and isolated layers (at infinite spacing, at which the interlayer interaction becomes vanishingly small) is

$$\begin{aligned} \beta \Delta F/V &= (1/2) \int \frac{d^3 q}{(2\pi)^3} \log \left(\frac{Bq_z^2 + Kq_\perp^4}{Kq_\perp^4} \right) \\ &= \frac{1}{2(2\pi)^2} \int_{-\infty}^{\infty} dq_z \int_0^{\infty} q_\perp dq_\perp \log \left(\frac{q_z^2/\lambda^2 + q_\perp^4}{q_\perp^4} \right) \end{aligned} \quad (5.3.15)$$

in which we have defined $\lambda^2 = K/B$.

Performing the integrals

To perform this integral, we use a trick. Focusing on the integral with respect to q_\perp first, write $x = q_z^2/\lambda^2$ and take the derivative with respect to x ; this leads to a simpler inner integral,

$$\begin{aligned} I' &= \int_0^\infty \frac{q dq}{x + q^4} \\ &= (1/4) \int_{-\infty}^\infty \frac{dy}{x + y^2} \\ &= \frac{\pi}{4\sqrt{x}} \end{aligned} \tag{5.3.16}$$

This we integrate with respect to x to find the inner integral we actually wanted,

$$I = \int_0^x I'(x) dx = \frac{\pi}{2} \sqrt{x} = \frac{\pi q_z}{2\lambda} \tag{5.3.17}$$

Now we perform the outer integral,

$$\begin{aligned} \beta \Delta F/V &= \frac{1}{2(2\pi)^2} \int_{-\Lambda}^\Lambda dq_z \frac{\pi q_z}{2\lambda} \\ &= \frac{1}{8\pi\lambda} \int_0^\Lambda q_z dq_z \\ &= \frac{\Lambda^2}{16\pi\lambda} \\ &= \frac{\pi}{16d^2} \sqrt{\frac{B}{K}} \end{aligned} \tag{5.3.18}$$

In the above, we have introduced a short-distance cutoff Λ on the wavenumbers in the z direction, without which the integral would diverge from contributions of unphysically short length scales. We have chosen $\Lambda = \pi/d$, so that $\cos(\pi z/d)$ is the fastest possible variation for $h(z)$. (This is sensible, because then alternating layers at $z = d, 2d, 3d, \dots$ are displaced alternately up and down.)

Imposing self-consistency

Now we impose a self-consistency condition, which relates the phenomenological coefficient B we have assumed in computing the layer fluctuations, to the compressibility of the system of stacked layers in the z direction.

From the results of the previous section, we have an expression for F/V , although we must be careful to identify all the d dependence, in $B(d)$ and from $K = k/d$. We do not yet know $B(d)$, so at first sight one may wonder how can we evaluate derivatives of F/V with respect to d . This is most easily dealt with by guessing that $B(d)$ will scale as some power of d , i.e., $B = B_0 d^{-\alpha}$, which can be substituted on both sides of the self-consistency relation.

In this way, it is easy to see that $\alpha = 3$, consistent with our initial scaling argument for B , whereupon we can compute B_0 . The final result is

$$B = \frac{9\pi^2 T^2}{64d^3 k} \tag{5.3.19}$$

with a corresponding result for the free energy per unit volume

$$\Delta F/V = \frac{3\pi^2 T^2}{128d^3 k} \tag{5.3.20}$$

Another more direct way to estimate the Helfrich modulus B is to adjust the value such that the variation in the spacing of adjacent layers is of order d . To do this, we evaluate

$$\begin{aligned}
\langle \Delta h^2 \rangle &= d^2 \langle (\partial_z h)^2 \rangle \\
&= \int \frac{d^3 q}{(2\pi)^3} \frac{T q_z^2}{B q_z^2 + K q_\perp^4} \\
&= \frac{T}{(2\pi)^2 k} \int_{-\infty}^{\infty} dq_z q_z^2 \int_0^{\infty} \frac{q_\perp dq_\perp}{q_z^2/\lambda^2 + q_\perp^4} \\
&= \frac{T}{4(2\pi)^2 k} \int_{-\infty}^{\infty} dq_z q_z^2 \int_{-\infty}^{\infty} \frac{dy}{q_z^2/\lambda^2 + y^2} \\
&= \frac{T}{4(2\pi)^2 k} \int_{-\infty}^{\infty} dq_z q_z^2 \frac{\pi}{|q_z/\lambda|} \\
&= \frac{T\lambda}{8\pi k} \int_0^\Lambda dq_z q_z \\
&= \frac{T\pi\lambda}{16d^2 k}
\end{aligned} \tag{5.3.21}$$

in which we have taken the same upper cutoff value $\Lambda = \pi/d$ as before.

Now if we impose $\langle \Delta h^2 \rangle$ equal to μd^2 , substitute $\lambda = \sqrt{K/B}$, $K = k/d$, and solve for B , we have

$$B = \frac{\pi^2 T^2}{256 \mu^2 d^3 k} \tag{5.3.22}$$

which result scales the same as our previous expression for B . (If we choose the value $\mu = 3/2$ — for which there is no particular justification — we arrive at precisely the same result as before.)

Unbinding transition

Now we consider a concentrated lamellar phase swelling under the influence of Helfrich repulsions, to which we add increasing amounts of liquid. How far will the lamellar phase swell? From our result for B , we see that when the phase is concentrated, the mutual repulsion of the layers is quite strong, but as the phase takes up more liquid the repulsion weakens. Suppose there is in addition a weak attractive interaction between the layers, from dispersive (van der Waals) forces. How will this limit the swelling of the lamellar phase?

This question is analogous to our earlier consideration of the swelling of a polymer chain in good solvent, except that in the present case, the entropic contribution gives rise to layer repulsion and the energetic contribution draws the layers closer together. To predict the extent of the swelling, we construct a Flory theory.

At first sight, we might be tempted to write the Flory theory in terms of the mean spacing d between layers, and find the optimum layer spacing by minimizing with respect to d . But the repulsion arises from adjacent layers undergoing fluctuations of order d , so we expect the layer spacing to be rather ill-defined. Certainly the attractive interaction between layers should not be evaluated at this separation exclusively. Instead, we write the Flory theory in terms of the interface volume fraction $\phi = \delta/d$; in terms of ϕ , we have

$$F/V = \frac{3\pi^2 T^2}{128 k \delta^3} \phi^3 - T \chi \phi^2 \tag{5.3.23}$$

In the above, the first term is the Helfrich repulsion; the second term is an estimate of the attractive energy, in which we have assumed that the concentration of layers is uniformly smeared

out in the z direction, much as we assume random locations of solutes in a lattice-gas estimate of attractive energies, or random locations of molecules in the van der Waals correction to the free energy of a liquid. The coefficient χ is a phenomenological measure of the attractive interactions between the layers; as we achieve better index matching between the layers and surrounding liquid, χ decreases to zero.

For a given value of χ , we can minimize the free energy with respect to ϕ to find the optimum layer concentration (and hence the average layer spacing, via $d = \delta/\phi$). If we specify a given average $\bar{\phi}$ (by the amount of surfactant and liquid we place into the system), we will either have a single lamellar phase (if $\bar{\phi}$ is more concentrated than the optimum ϕ^*), or a coexistence of a lamellar phase at ϕ^* with excess liquid (if $\bar{\phi} < \phi^*$). We find that ϕ^* is linear in χ , resulting in a phase diagram as shown in the figure.

As written, this simple model predicts a “critical unbinding” transition as χ vanishes, the optimum layer spacing diverges, and the first-order transition between bound layers at ϕ^* and excess liquid (equivalently, unbound layers at infinite dilution) reaches a critical endpoint. In reality, when the layer spacing swells to of order the persistence length of the membranes, we expect the lamellar phase should transform into a sponge phase, analogous to a bicontinuous microemulsion but with the same liquid on each side of the bilayer.

5.4 Dynamics of interfaces and vesicles

In this lecture, we introduce simple qualitative and scaling arguments to describe the dynamics of fluctuations of a planar interface. The customary way to analyze such motions is to set up and solve the appropriate form of the Navier-Stokes equation. However, just as it is a useful first step in equilibrium statistical mechanics to construct scaling arguments to inform our intuition and constrain the answer of more exact calculations, it is helpful to develop scaling arguments to describe dynamics.

Consider a sinusoidal modulation of the height of an interface between a liquid (water, say) and air, partly or completely saturated with surfactant. How does the interface evolve in time from such an initial state? There are three driving forces that push the interfacial shape back towards its lowest-energy state (flat). These are 1) gravity, 2) surface tension, and 3) bending stiffness.

These forces may accelerate the fluid underneath the interface sufficiently to cause the shape of the interface to overshoot the flat state, leading to an oscillation. For an inviscid fluid (without viscosity), there is no mechanism for the initial energy of the surface deformation to be dissipated, and the oscillation persists indefinitely. With viscosity, the oscillation will damp out at some rate.

Our general approach will be to first estimate the oscillation frequency without dissipation, then to estimate the rate at which the energy will be dissipated. This we do by equating estimates of the potential energy to the kinetic energy — oscillations without dissipation conserve energy, which periodically swaps between potential and kinetic.

If the dissipation rate is small compared to the lossless oscillation frequency, then this approach is consistent — the mode will indeed oscillate and slowly dissipate. If on the other hand the dissipation rate turns out to be large compared to the frequency, we must start over, and treat the relaxation of the interfacial wave in the “overdamped” limit, in which we neglect the inertia of the fluid, and determine the relaxation rate by comparing the dissipation rate with the energy stored in the mode.

Driving forces

Given a surface wave of amplitude h and wavelength λ , we need to estimate the potential energy stored in the wave, for each of the three different possible driving forces (all of which are present in principle for a given surface wave).

For bending, we recall the energy per unit area takes the form $(k/2)(\nabla^2 h)^2$ in the small-amplitude approximation; here, we assert that the gradients will be of order $1/\lambda$ (or equivalently of order q), so that the energy per unit area is of order $kq^4 h^2$.

For surface tension, we write the energy per unit area as

$$U/A \sim \gamma \sqrt{1 + (\nabla h)^2} \approx (\gamma/2)(\nabla h)^2 \quad (5.4.1)$$

in which we have used the result from calculus for the surface area of a height function, and expanded assuming a small-amplitude wave. Correspondingly, the energy per unit area from interfacial tension will be of order $\gamma q^2 h^2$.

Finally, for gravity, the energy per unit area is the gravitational potential energy of lifting fluid volume elements from the troughs to the crests of the wave. We write

$$U/A \sim \int_0^h dz \rho g h = \rho g h^2 / 2 \quad (5.4.2)$$

so that the energy per unit area from gravity scales as $\rho g h^2$.

Summarizing, we have potential energy per unit area of

$$U/A \sim \begin{cases} kq^4h^2 & \text{bending} \\ \gamma q^2h^2 & \text{tension} \\ \rho gh^2 & \text{gravity} \end{cases} \quad (5.4.3)$$

Kinetic energy

To estimate the kinetic energy, we need to know how large is the typical velocity, and how deep into the fluid underlying the interface the velocity field persists. The velocity at the interface we expect to be of order $h\omega$, where ω is the oscillation frequency (since the surface moves up and down a distance h in one period).

The velocity penetrates a depth of order the wavelength into the fluid. Here we argue by dimensional analysis, and the requirement that the penetration length should not depend on the amplitude h , since we are in a linear response regime, and the velocity field should be proportional to the amplitude of the wave. Thus the mass per unit area of fluid involved in the motion is of order $\rho\lambda$ or ρ/q . The kinetic energy per unit area is then of order

$$U/A \sim (\rho/q)(h\omega)^2 \quad (5.4.4)$$

Dispersion relations; crossovers

Equating the kinetic and potential energies, we arrive at the following scaling results for the dispersion relation (i.e., relation $\omega(q)$ between frequency of a wave and its wavenumber):

$$\omega^2 \sim \begin{cases} (k/\rho)q^5 & \text{bending} \\ (\gamma/\rho)q^3 & \text{tension} \\ gq & \text{gravity} \end{cases} \quad (5.4.5)$$

If an interface has significant contributions from more than one of these driving forces, then the dispersion relation for waves on such an interface will be more complicated. But since the dispersion relations from the different driving forces scale differently with wavenumber, we can find crossover wavenumbers that mark the boundary between regions where one driving force is dominantly larger than another.

For example, for an interface with both interfacial tension and gravity acting, we can find $q_{g \rightarrow \gamma} \sim (g\rho/\gamma)^{1/2}$. The notation “ $g \rightarrow \gamma$ ” signifies that as we increase the wavenumber, the dominant driving force crosses over from g to γ , i.e., from gravity to interfacial tension. The full set of these crossover length scales is

$$\begin{aligned} q_{g \rightarrow \gamma} &\sim (g\rho/\gamma)^{1/2} \\ q_{\gamma \rightarrow k} &\sim (\gamma/k)^{1/2} \\ q_{g \rightarrow k} &\sim (g\rho/k)^{1/4} \end{aligned} \quad (5.4.6)$$

For a quick estimate, we take values for the coefficients as follows (CGS units):

$$\begin{aligned} g &\approx 1000 \\ \gamma &\approx 10 \\ \rho &\approx 1 \\ k &\approx 20kT \approx 10^{-13} \end{aligned} \quad (5.4.7)$$

The corresponding values for the crossover length scales are

$$\begin{aligned} q_{g \rightarrow \gamma}^{-1} &\approx 0.1 \text{ cm} \\ q_{\gamma \rightarrow k}^{-1} &\approx 10 \text{ \AA} \\ q_{g \rightarrow k}^{-1} &1 \mu \end{aligned} \quad (5.4.8)$$

Thus for garden variety values of the coefficients, gravity waves become “capillary” waves (driven by interfacial tension) at wavelengths shorter than 1mm, whereas capillary waves become bending waves at only extremely short wavelengths of order 10Å.

Dissipation

Now we estimate the rate at which the energy of the surface wave is dissipated by the fluid viscosity. The viscous stresses are of the form $\eta(\nabla_i v_j + \nabla_j v_i)$, and stress times strain rate gives the rate of work done against dissipation, so that the dissipation scales as

$$\dot{E}/V \sim \eta(\nabla v)^2 \quad (5.4.9)$$

We need a scaling for the dissipation of energy per unit area, for which we multiply by λ , our estimate for the depth to which the velocity field penetrates. The result is

$$\dot{E}/A \sim \eta(\omega h)^2 q \quad (5.4.10)$$

We convert this to a decay rate by dividing by the energy per unit area itself; to keep things simple, we divide by our estimate for the kinetic energy only, with the justification that the kinetic and potential energies are of the same order of magnitude in an oscillator. This approach allows us to write a scaling result for the decay rate Γ of the energy independent of the nature of the driving force:

$$\Gamma \sim (\eta/\rho)q^2 \quad (5.4.11)$$

Now we can compare this energy decay rate to the oscillation frequency. The ratio $Q = \omega/\Gamma$ is the “quality factor” of the oscillation (the precise definition may differ by a numerical prefactor). If Q is large, the oscillation decays slowly, over many periods; if Q is of order unity or less, the oscillation decays quickly, and the mode is not well defined. We have

$$1/Q^2 \sim (\Gamma/\omega)^2 \begin{cases} (\eta^2/\rho k)q^{-1} & \text{bending} \\ (\eta^2/\rho\gamma)q & \text{tension} \\ (\eta^2/\rho^2 g)q^3 & \text{gravity} \end{cases} \quad (5.4.12)$$

Note that for capillary or gravity waves, Q increases as q decreases; long wavelength modes are less damped and better defined. In contrast, for bending waves, Q decreases as q decreases, implying that long wavelength modes will be overdamped.

Evidently, the condition Q of order unity determines a set of “cutoff wavenumbers” for surface waves, under the assumption they are driven by bending, tension, or gravity. The results are

$$\begin{aligned} q_k^* &\sim \eta^2/\rho k \\ q_\gamma^* &\sim \gamma\rho/\eta^2 \\ q_g^* &\sim (g\rho^2/\eta^2)^{1/3} \end{aligned} \quad (5.4.13)$$

With the typical value of viscosity of 10^{-2} (CGS units), we have typical values for the crossover wavelengths of

$$\begin{aligned} 1/q_k^* &\approx 0.1\text{\AA} \\ 1/q_\gamma^* &\approx 0.1\mu \\ 1/q_g^* &\approx 0.01\text{cm} \end{aligned} \tag{5.4.14}$$

We find that essentially all bending modes will be overdamped (have Q less than unity), whereas capillary waves will be underdamped (have Q larger than unity) for wavelengths longer than 0.1μ , and gravity waves will likewise be underdamped for wavelengths longer than 0.01cm .

Overdamped relaxation

We showed above that the dynamics of surface waves driven by bending are typically overdamped, in contrast to capillary or gravity waves. For overdamped waves, inertia is irrelevant; the wave relaxes by “creeping flow” of the velocity field, in which the viscous stresses in the fluid balance against the surface stresses driving the flow. The wave amplitude decays exponentially, and does not overshoot.

The simplest way to estimate the relaxation rate ω for the wave is to combine our estimate of the dissipation rate for the energy per unit area with our estimate of the initial potential energy of the wave, to self-consistently determine the relaxation rate. That is,

$$\omega \sim \frac{\dot{E}/A}{E/A} \sim \frac{\eta(\omega h)^2 q}{kq^4 h^2} \tag{5.4.15}$$

which implies

$$\omega \sim kq^3/\eta \tag{5.4.16}$$

(This result can also be obtained by equating scaling estimates for the force per unit area at the surface, and the viscous stress at the surface.)

Bending modes can be observed in a microscope on the surfaces of vesicles or red blood cells, where they appear as “flicker”, slowly relaxing large amplitude changes in shape. The amplitudes of low- q modes are large because the energy cost is small; we recall that $\langle h_q^2 \rangle$ scales as $T/(kq^4)$, which means that the long-wavelength modes also have large amplitudes.