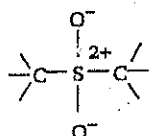
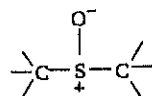
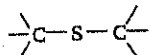
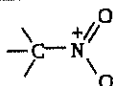
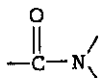
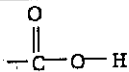


The bulk phases of matter

Functional group



(M - metal)

1.1 Gases, liquids and solids

The three most common states, or *phases*, of matter, *gases*, *liquids* and *solids* are very familiar (Walton, 1976). Phases that are not so well known are *plasmas* and *liquid crystals* (although these are both found in electrical and electronic devices in everyday use). All these states are generally distinguished by the degree of *translational* and *orientational order* of the constituent molecules. On this basis some phases may be further subdivided. For example, solids, consisting of a rigid arrangement of molecules, can be *crystalline* or *amorphous*. In an amorphous solid (a good example is a glass), the molecules are fixed in place, but with no pattern in their arrangement. As shown in figure 1.1, the crystalline solid state is characterized by long-range translational order of the constituent molecules (the molecules are constrained to occupy specific positions in space) and long-range orientational order (the molecules orient themselves with respect to each other). The molecules are, of course, in a constant state of thermal agitation, with a mean translational kinetic energy of $3kT/2$ (k is Boltzmann's constant, T is temperature; $kT/2$ for each component of their velocity). However, this energy is considerably less than that associated with the chemical bonds in the material and the motion does not disrupt the highly ordered molecular arrangement.

In the gaseous state, the intermolecular forces are not strong enough to hold the molecules together. They are therefore free to diffuse about randomly, spreading evenly throughout any container they occupy, no matter how large it is. The average interatomic distance is determined by the number of molecules and the size of the container. A gas is easily compressed, as it takes comparatively little force to move the molecules closer together.

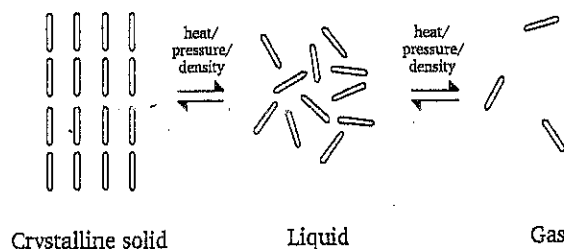


Figure 1.1 The three most common bulk phases of matter.

On the microscopic level, the liquid state is generally thought of as a phase that is somewhere between that of a solid and that of a gas. The molecules in a liquid neither occupy a specific average position nor remain oriented in a particular way. They are free to move around and, as in the gaseous state, this motion is random. The physical properties of both liquids and gases are *isotropic*; i.e., they do not depend upon direction (direction-dependent properties are called *anisotropic*). Therefore, there is a similarity between liquids and gases and under certain conditions it is impossible to distinguish between these two states. When placed in a container, the liquid will fill it to the level of a free surface. Liquids flow and change their shape in response to weak outside forces. The forces holding a liquid together are much less than those in a solid. Liquids are highly incompressible, a characteristic that is exploited in hydraulic systems.

Almost all elements and chemical compounds possess a solid, a liquid and a gaseous phase. The gaseous phase is favoured by high temperatures and low pressures. A transition from one phase to another can be provoked by a change in temperature, pressure, density or volume.

1.2 Liquid crystals

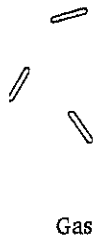
The melting of a solid is normally a very sharp transition. As the material is heated, the order of the system abruptly changes from that of the three-dimensional order of the solid to the zero order associated with the liquid. However, it is not uncommon for an *organic* solid to pass through intermediate phases as it is heated from a solid to a liquid. Perhaps one in every few hundred organic compounds exhibits such behaviour. Such phases are known as *mesophases*. When such a state is formed, the translational order of the solid phase may be lost, but the orientational order remains. The resulting phase is termed a *thermotropic liquid crystal* (Collings, 1990). Sometimes a mesophase may display translational order but no orientational order; this is termed a *plastic crystal*. A very wide range of liquid crystal phases is now known. These are identified by the degree of short range translational order and by the shape of the molecules.

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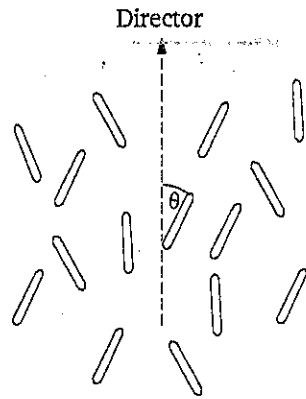


Figure 1.2 Arrangement of rod-shaped molecules in a liquid crystalline phase. Each molecule makes an angle of θ with the director.

The *nematic* (from the Greek word for thread) phase is the least ordered liquid crystal phase and is exploited extensively in electrooptic applications. This phase has no long-range translational order and only orientational order. There is only one nematic phase and, on heating, this will eventually become an isotropic liquid. A schematic diagram, showing the arrangement of rod-shaped molecules in a nematic phase, is given in figure 1.2. The molecules in the liquid crystal are free to move about in much the same fashion as in a liquid; as they do so they tend to remain orientated in a certain direction. The direction of preferred orientation is called the *director* of the liquid crystal. Each molecule is oriented at some angle θ about the director. The degree of orientational order is given by the *order parameter* S which is defined

liquid crystal $S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$ orientational order (1.1)

A value of $S = 1$ indicates perfect orientational order whereas no orientational order results in $S = 0$.

Smectic (from the Greek word for soap) phases are usually formed by thermotropic liquid crystals at lower temperature than the nematic phase. Besides the orientational order, smectic phases possess one-dimensional translational ordering into layers. The smectic phases can be further subdivided and, at present, twelve different types have been identified. These are designated S_A, S_B, \dots, S_K ; there are two smectic S_B phases – the *crystal B* and *hexatic* (for a discussion of this phase, see Tredgold 1994) S_B phases. Some of these mesophases (crystal B, S_E, S_G, S_H and S_J) have very long-range correlation of position over many layers and are more similar to crystalline solids.

The S_A phase is the least ordered of the thermotropic smectic phases. The molecules are arranged in disordered layers, each layer having a liquid-like

they move as liquid

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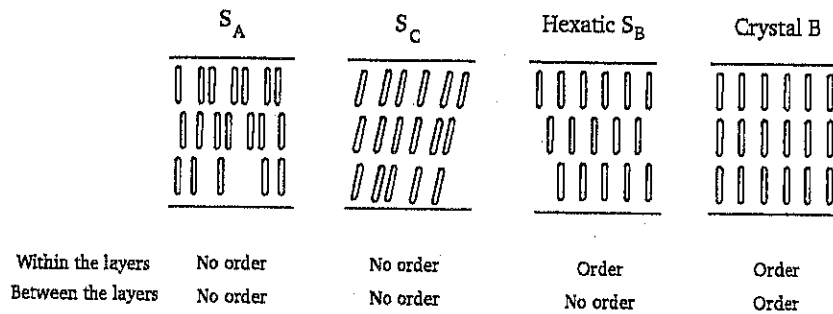


Figure 1.3 Different smectic liquid crystalline arrangements of rod-shaped molecules. S_C is a tilted version of S_A .

freedom of motion of its constituent molecules in two dimensions, with the director perpendicular to the layer planes. By contrast, in the S_C phase the molecules are tilted from this direction by about 35° . This tilt is correlated between molecules within each layer and from one layer to another. In the hexatic S_B phase, there is again ordering of orientationally aligned molecules into layers. The molecules are arranged in a hexagonal array but the translational order is short-range only. The orientation of the hexagonal net is, however, maintained over a long range and unlike the ordering of molecular positions, is correlated between layers. Two tilted variations of the S_B phase exist in which the tilt direction is constrained to point either towards one face of the hexagonal lattice (S_F) or towards one apex (S_I). The S_A , S_C , hexatic S_B and crystal B arrangements of rod-shaped molecules are contrasted in figure 1.3 (Lacey, 1994). Further details about these smectic liquid crystal phases are to be found in the book by Gray and Goodby (1984).

The final distinct type of liquid crystalline mesophase is the *cholesteric* or *chiral nematic*. The molecules in such a phase are arranged in a unique helical structure in which the director gradually rotates from one plane of molecules to the next. Such phases can exhibit vivid colour effects that change with temperature (as the pitch of the helix changes) and are exploited as temperature sensors. These molecules may also form smectic phases.

1.3 Phase changes

The science of thermodynamics allows the properties of the various phases of matter to be correlated. The *state* of any thermodynamic system (e.g., a fixed amount of matter) is specified by values of certain experimentally variable quantities called *state variables* or *properties*. Familiar examples are the temperature of a system, its pressure and the volume occupied by it. Those properties that are proportional to the mass of the system are called *extensive*; examples are the total volume and total energy of the

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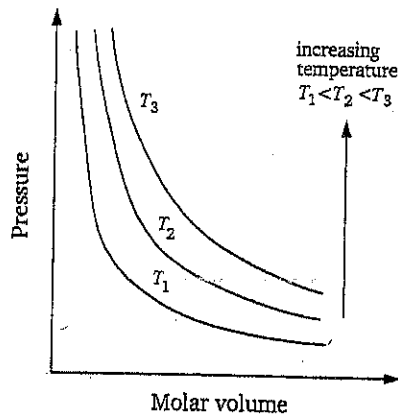


Figure 1.4 Pressure versus molar volume isotherms for an ideal gas.

system. Properties such as temperature or density, which are independent of mass, are called *intensive*.

It is found by experiment that only a certain minimum number of the properties of a pure substance can be given an arbitrary value. The values of the remaining properties are then determined by the nature of the substance. For example, suppose that nitrogen gas is allowed to flow into an evacuated tank at a constant temperature T . The volume V of the gas admitted is then fixed by the volume of the tank and the number of moles n of gas is fixed by the amount that is admitted. Once T , V and n have been fixed, the pressure P is determined by the nature of nitrogen and cannot be given any arbitrary value. It follows that there exists a certain relation between the properties P , V , T and n . This relation is termed an *equation of state* and, for an ideal gas, may be written

$$Pv = RT = N_A k T \quad (1.2)$$

where R is the *universal gas constant* ($R = 8.314 \times 10^3 \text{ J kilomole}^{-1} \text{ K}^{-1}$), N_A is Avogadro's number ($N_A = 6.022 \times 10^{26} \text{ kilomole}^{-1}$) and v is the *specific molar volume* (i.e., $v = V/n$). Boltzmann's constant, k ($k = 1.381 \times 10^{-23} \text{ J K}^{-1}$) may be thought of as the *universal gas constant per molecule* (i.e., $k = R/N_A$).

Figure 1.4 shows a series of pressure versus volume plots for an ideal gas at different temperatures. The curves are simple hyperbolas and are called *isotherms*. It is also convenient to plot the values of P , v and T to form a three-dimensional graph. For a real substance, such a representation will include data over the liquid and solid phase regions. Such a diagram, for a substance that contracts on freezing (e.g., carbon dioxide), is shown in figure 1.5; this is known as a *phase diagram*. The figure reveals that there are certain regions (i.e., certain ranges of the variables P , v and T) in which

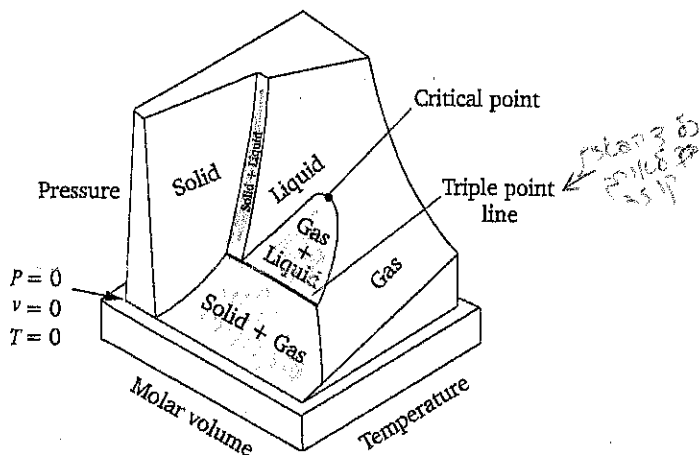


Figure 1.5 Pressure versus molar volume versus temperature plot for a substance that contracts on freezing.

the substance can exist in a single phase only; these are labelled solid, liquid and gas. In other regions, labelled solid + gas, solid + liquid and gas + liquid, two phases can exist simultaneously. All three phases exist along a line known as the triple point line. At a particular point called the critical point, the specific molar volumes of the liquid and gas become equal and it is no longer possible to distinguish one of these phases from the other.

Equations of state may also be written for both the liquid and the solid regions of the phase diagram shown in figure 1.5. For example, the following expression, derived by van der Waals, may apply to both the liquid and gaseous regions

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (1.3)$$

a and b are constants for any one gas/liquid: the term a/v^2 arises from the existence of intermolecular forces and the constant b is proportional to the volume occupied by the molecules themselves. In the case of a solid, a simple equation of state might be

$$v = l + mT + nP \quad (1.4)$$

where l , m and n are empirically determined constants.

Isotherms for a real substance can be obtained by projecting the v - P - T surface onto the pressure-volume plane. Figure 1.6 is such a construction, illustrating what occurs as the specific molar volume of a material is reduced, taking it from the gaseous state to its solid phase. Curves are shown at three different temperatures. At temperature T_2 , the first stage of the process

Figure 1.4
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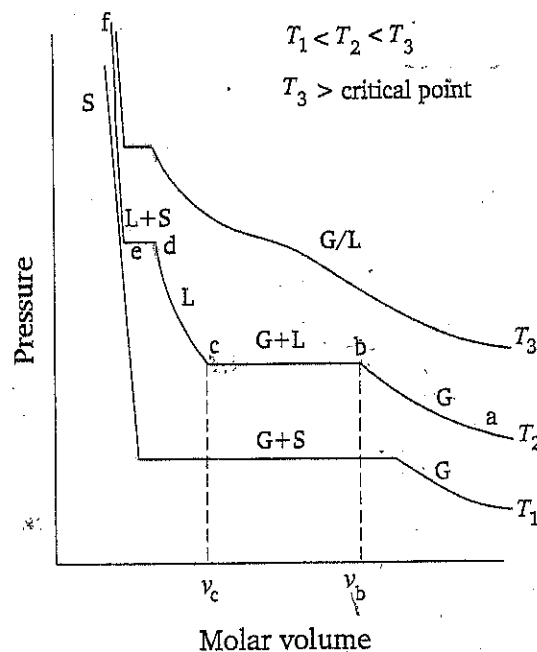


Figure 1.6 Pressure versus molar volume isotherms at three different temperatures for a bulk material.

(a \rightarrow b in the figure) is the isothermal compression of the gas. If the gas is ideal, the P versus v curve will be a simple hyperbola, as shown in figure 1.4. At point b the gas begins to condense to a liquid. The pressure remains constant until point c is reached, when all the gas has condensed. Between the pure gas state at b and the pure liquid state at c, the ratio of the mass of gas present (G) to the total mass of gas and liquid (G + L) decreases linearly from one to zero. The proportion by mass should not be confused with the proportion by volume. Throughout the change from b to c, the molar volume of the gas is v_b and that of the liquid is v_c . Further reduction in volume of the liquid phase causes the appearance of solid particles at point d. Solidification (at constant pressure) is complete at point e at which only single phase solid is present. Curve e \rightarrow f therefore represents the compression of the solid phase. Note that if the compression takes place at a temperature above the critical point (i.e., at T_3 in figure 1.6), the distinct phase change corresponding to the condensation of the gas to the liquid is not observed; the gas and liquid phases are now inseparable. On the other hand, if the temperature is reduced sufficiently (i.e., to T_1), then the gas transforms directly into a solid.

Phase changes, such as solidification or vaporization, which take place at constant temperature, are accompanied by heat absorption or evolution.

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the liquid and the solid. In example, the following both the liquid and

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projecting the v - P - T surface. In such a construction, the v - P surface of a material is reduced, and the phase changes are shown at three stages of the process

This heat is commonly known as the *latent heat* of the transformation. However, in the strict thermodynamic sense, this is the *enthalpy* H given by

$$H = U + PV \quad (1.5)$$

where the first term, U , on the right-hand side of the equation is the *internal energy*. This is simply the sum of all the potential and kinetic energies in a system. The above relation shows that the enthalpy associated with any phase change consists of two distinct parts. For example, when a liquid vaporizes at its boiling point, energy is required not only to break the bonds between molecules in the liquid (the U term) but also to 'push back' the atmosphere to make room for the vapour (the PV term). The horizontal (constant pressure) lines on the isotherms in figure 1.6 are associated with enthalpy changes as the phase transforms from gas to liquid ($b \rightarrow c$) or from liquid to solid ($d \rightarrow e$). At the critical temperature, the enthalpy for vaporization becomes zero.

1.4 Thermodynamic equilibrium

When an arbitrary system is left to itself, its properties (P , V , T etc.) will generally change. However, after a sufficiently long period, the properties will be invariant with time. This final state will depend on the nature of the system. For example, a simple mechanical arrangement, such as a ball rolling down a hill, consistently comes to rest in the state of lowest energy (i.e., with the ball at the bottom of the hill). Any thermodynamic system, left for long enough, will reach a state of *thermodynamic equilibrium*. Here, thermodynamic equilibrium is achieved when the *free energy* is minimized. For systems at constant volume, this is given by the *Helmholtz function* F

$$F = U - TS \quad (1.6)$$

and for constant pressure changes, the free energy is given by the *Gibbs' function* G

$$G = H - TS = U + PV - TS \quad (1.7)$$

In both the above equations, S is the *entropy*. Classically this is the heat into, or out of, the system divided by temperature. For a simple phase change

$$\Delta S = \frac{\Delta H}{T} \quad (1.8)$$

Entropy is also a measure of the disorder of a thermodynamic system. The specific molar entropy change ($\Delta S/n$) for vaporization is normally much greater than that for fusion, confirming the increased disorder produced in the former phase transformation.

Equations (1.6) by reducing the temperature, the transition to the free energy. As a result, the temperature the they constitute

Many states of thermodynamic equilibrium slowly (e.g., an order and non-order and non-order) a supercooled liquid measurable properties appropriate to a true equilibrium

textbooks (e.g., Thermodynamics) order and non-order Gibbs' function first derivative that of melting simply equal to thermodynamic derivative are constant. In such transition specific volume the critical point of a superconductor zero magnetic

1.5 Phase rule

A very useful phase rule written

where P is the pressure, T the system temperature, C the number of components (the system).

Equations (1.6) and (1.7) reveal that free energy can be minimized either by reducing the internal energy or by increasing the entropy term. At low temperature, the internal energy of the molecules makes the greater contribution to the free energy, and so the solid phase is the favoured state. At higher temperature the entropy of the system becomes the predominant influence. As a result, the fluid phases are stable at elevated temperatures although they constitute higher internal energy configurations than the solid phase.

Many states of matter that are commonly encountered are not in a true state of thermodynamic equilibrium. Equilibrium may be approached very slowly (e.g., an amorphous glass will eventually crystallize over a period of many hundreds of years) or the system may be in a *metastable* state (e.g., a supercooled liquid or vapour). However, as such systems will have directly measurable properties (P , H , S etc.) that are stable during an experiment, it is appropriate to assume these properties can be related in the same way as for a true equilibrium state. A discussion on this topic may be found in many textbooks (e.g., Sears and Salinger, 1975).

Thermodynamically, phase changes of matter can be divided into *first-order* and *higher-order transitions*. In the former case, the specific molar Gibbs' function g ($= G/n$) is continuous but there is a discontinuity in the first derivative of g across the transition. An example of such a change is that of melting or evaporation: in these cases the discontinuity in $\partial g/\partial T$ is simply equal to the entropy of transformation ($\Delta H/T$). For second-order thermodynamic transitions, both the specific Gibbs' function and its first derivative are continuous, but the second derivative changes discontinuously. In such transitions, the enthalpy of transformation is zero and the molar specific volume does not change. The transition of a liquid to a vapour at the critical point, ferromagnetic to paramagnetic transitions and the change of a superconductor from the superconducting state to the normal state in zero magnetic field are examples of second-order phase transitions.

1.5 Phase rule

A very useful tool for predicting equilibrium-phase relationships is the *Gibbs' phase rule* (Ferguson and Jones, 1973; Sears and Salinger, 1975). This can be written

$$F = C - P + 2 \quad (1.9)$$

where P is the number of phases and F is the number of *degrees of freedom* the system possesses. The latter quantity is simply the number of state variables (T , V , P etc.) that can be *independently* changed. The number of *components* (C) can be thought of as the number of 'pure' substances in the system. A formal definition (and precise definitions are extremely

important in thermodynamics) is that the number of components is the minimum number of molecular species in terms of which the compositions of all the phases may be quantitatively expressed (Ferguson and Jones, 1973). Equation (1.9) relates to all macroscopic systems influenced only by changes in pressure, temperature and concentration.

The application of the phase rule may be illustrated by reference to the isotherm at temperature T_2 in figure 1.6. Here a single pure material ($C = 1$) is held at a constant temperature. In the gaseous phase region ($P = 1$), the pressure or the volume of the gas may be changed. These are not independent quantities as they are related by an equation such as (1.2); if the pressure is changed, then the volume of the gas will also change. The temperature, of course, is an additional degree of freedom. Therefore, for the single component, single phase system, $F = 2$, as predicted by equation (1.9). As the gas is compressed, the liquid state will appear; i.e., $P = 2$. The phase rule indicates that the thermodynamic system must lose one of its degrees of freedom ($F = 1$). The temperature has already been fixed; the pressure must therefore remain constant during the gas to liquid phase transformation. The pressure (or temperature) can vary again when all the gas has condensed into the liquid state. A similar argument may be used to explain the constant pressure region in the liquid to solid phase change in figure 1.6. If a single component system is held at constant pressure, rather than at a fixed temperature, then the phase rule may also be used to account for the familiar observation of a constant temperature during a gas to liquid or liquid to solid transformation.

If three phases of a single component system are in equilibrium, then the system has no degrees of freedom. This occurs along the triple point line in the full phase diagram shown in figure 1.5. At first sight, it might be thought that such a system has a single degree of freedom (the molar volume) as the gas/liquid/solid is in equilibrium along a line in this three-dimensional plot. However, it is only the relative composition of the phases that change along this line; the specific molar volumes of the three phases are fixed. The temperature and pressure of the triple point of a pure substance are uniquely defined and this is often used as a fixed point on a thermodynamic temperature scale.

The ideas developed in this chapter have concerned the relationships between the bulk phases of matter. However, many of the concepts are quite general and, as will be shown in chapter 2, may be equally well applied to the states of a monomolecular film.

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2

Monolayers: two-dimensional phases

2.1 The gas-liquid interface

Certain organic molecules will orient themselves at the interface between a gaseous and a liquid phase (or between two liquid phases) to minimize their free energy. The resulting surface film is one molecule in thickness and is commonly called a *monomolecular layer* or simply a *monolayer*. In the previous chapter the individual properties of bulk phases were outlined. The interface region will now be examined.

The boundary between a liquid and a gas (e.g., the air/water interface) marks a transition between the composition and properties of the two bulk phases. A surface layer will exist with different properties from those of either bulk phase (Adamson, 1982; Gaines, 1966). The thickness of this region is very important. If the molecules are electrically neutral, then the forces between them will be short-range and the surface layer will be no more than one or two molecular diameters. In contrast, the Coulombic forces associated with charged species can extend the transition region over considerable distances.

The microscopic model of a real interface is one of dynamic molecular motion as molecules move in and out of it. However, for the interface to be in equilibrium, as many molecules must diffuse from the bulk of the liquid to its surface per unit time as leave the surface for the bulk. A molecule at the surface is surrounded by fewer molecules than one in the bulk liquid (see figure 2.1). Therefore, more molecules will diffuse initially from the surface, increasing the mean atomic separation (and therefore the intermolecular forces) between surface molecules. The activation energy for a surface molecule escaping into the bulk will then increase until it is equal to

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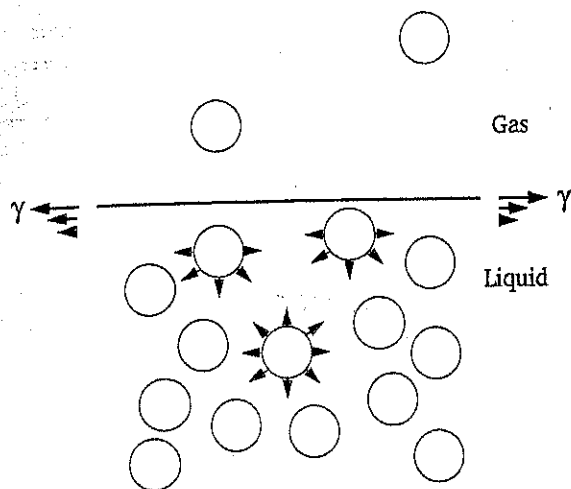


Figure 2.1 Forces experienced by molecules in the bulk of a liquid and at the liquid/gas interface.

that for molecules diffusing from the bulk to the surface, and a state of equilibrium is achieved. The line force acting on the surface molecules is the *surface tension* γ (Walton, 1976).

At thermodynamic equilibrium, the surface tension of a planar interface, can be shown to be related to the partial derivatives of the free energy functions, discussed in chapter 1, with respect to the area A of the surface (Birdi, 1989), i.e.,

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T,V,n_i} = \left(\frac{\partial G}{\partial A} \right)_{T,P,n_i} \quad (2.1)$$

When describing the thermodynamics of surfaces, it is common practice to introduce the concept of *excess* quantities (Birdi, 1989; Gaines, 1966). Therefore, the thermodynamic extensive state variables of the two bulk phases (e.g., number of moles, internal energy, entropy) are assumed to be constant up to an imaginary dividing surface and the excess quantities describe the properties of the surface. For a *pure* liquid in equilibrium with its saturated vapour at a planar interface, surface tension is equal to the excess Helmholtz free energy per unit area, i.e.,

$$\gamma = \frac{F^s}{A} \quad (2.2)$$

where F^s refers to the surface excess free energy. There is also an alternative approach to the thermodynamics of surfaces in which the surface region is considered as a separate phase (of small but finite volume) with its own values of extensive variables (Gaines, 1966).

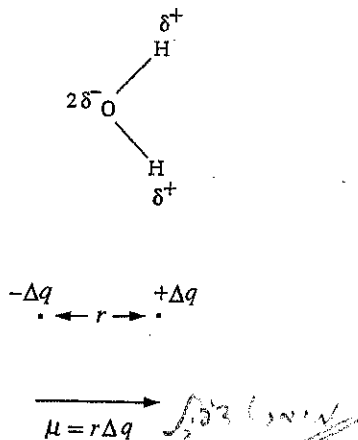


Figure 2.2 Origin of electric dipole moment, μ , in a water molecule.

Surface tension is analogous to vapour pressure, remaining constant for two phases in equilibrium if the temperature is constant, but changing with changing temperature. Unlike the vapour pressure, however, which increases with increasing temperature, γ decreases with increasing temperature and becomes zero at the critical point.

The presence of a monomolecular film on a liquid surface will affect the surface tension. In monolayer experiments it is normal to refer to a measurement of *surface pressure*. This pressure Π is equal to the reduction of the pure liquid surface tension by the film, i.e.,

$$\Pi = \gamma_0 - \gamma_{\text{film}} \quad (2.3)$$

where γ_0 is the surface tension of the pure liquid and γ is the surface tension of the film-covered surface. Monomolecular films have been studied on a variety of *subphase* (liquid) surfaces, for example, water, mercury and hydrocarbons. However, almost all the work on transferred monolayers (i.e., removed from the subphase surface and deposited onto solid supports) has concentrated on aqueous subphases. The discussion will therefore be restricted to this. Values of Π of the order of mN m^{-1} are generally encountered in monolayer studies on a water surface; the maximum value of Π is 72.8 mN m^{-1} at 20°C , the surface tension of water.

2.2 Monolayer materials

All compounds may be roughly divided into those that are soluble in water and those that do not dissolve. The former materials are generally *polar*, that is they carry an uneven distribution of charge. Associated with such molecules is an entity called a *dipole moment* μ . Figure 2.2 illustrates the case for a molecule of water. Each of the two hydrogen atoms shares an

$$\{\mu = r\Delta q\}$$

Table 2.1 Dipole moment

Chemical group

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NO ₂
NH ₂
CN
benzene ring
cis C=C
trans C=C

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Table 2.1 Dipole moments of various chemical groups.

Chemical group	Example	Dipole moment, μ [Debye]
OOH	propranoic acid (C_2H_5COOH)	1.75
OH	propanol (C_3H_7OH)	1.68
NO_2	nitropropane ($C_3H_7NO_2$)	3.66
NH_2	propylamine ($C_3H_7NH_2$)	1.17
CN	cyanoethane (C_2H_5CN)	4.02
benzene ring	(C_6H_6)	0
<i>cis</i> C=C	<i>cis</i> -2-butene	0.33
<i>trans</i> C=C	<i>trans</i> -2-butene	0

electron pair with the oxygen atom. The geometry of the shared electron pairs in the outer shell of the oxygen causes the molecule to be V-shaped. The strong electron-withdrawing tendency of the oxygen atom results in a local negative charge at the apex of the V, and gives the two hydrogen nuclei local positive charges. Although the water molecule is electrically neutral, its positive and negative charges are widely separated. If the water molecule is modelled as two equal and opposite charges $\pm\Delta q$ separated by a distance of r (constituting a dipole), then the magnitude of the dipole moment is given by the product of Δq and r . To be strictly correct, μ is a vector quantity, directed from negative to positive charge. The SI units of dipole moment are [Cm], however most workers use the *Debye unit* ($1D = 3.336 \times 10^{-30} \text{ C m}$); the dipole moment of water is 1.85 D. The solvent properties of water are related to the attraction between its electric dipoles and the charges associated with the solute. Dipole moments associated with chemical groups that are commonly encountered in monolayer work are given in table 2.1. Symmetrical molecules, such as benzene, possess a zero dipole moment. These substances do not readily dissolve in water and are termed *nonpolar*.

The molecules of most (but certainly not all) monolayer-forming materials are composed of two parts: one that by itself would mix with water and another that by itself would not. The soluble part is called *hydrophilic* (water-loving) and the insoluble part is termed *hydrophobic* (water-hating). These molecules are *amphiphiles*, the most important types of which are *soaps* and *phospholipids*. Such compounds are also called *surfactants*. A full discussion of the range of these compounds is given in chapter 4. However, at this point, it is appropriate to introduce the simplest substances of this type. Figure 2.3 shows the structure of a classical monolayer forming material, n-octadecanoic acid, commonly known as stearic acid - $C_{17}H_{35}COOH$. This is one of a series of long-chain fatty acids, with the general chemical formula $C_nH_{2n+1}COOH$. The n-octadecanoic acid molecule

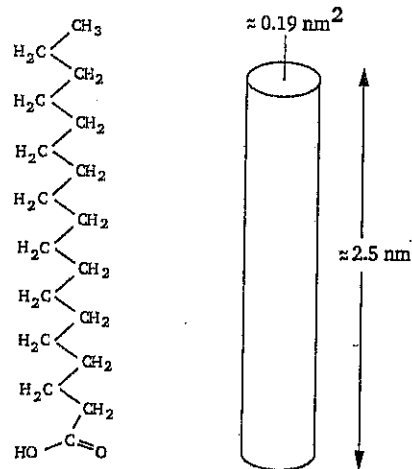


Figure 2.3 Chemical formula for n-octadecanoic acid (stearic acid). The approximate geometrical shape and dimensions of the molecule are shown on the right.

is cylindrical in shape, with a length of approximately 2.5 nm and a cross-section of about 0.19 nm². It consists of 16 CH₂ groups forming a long hydrocarbon chain with a methyl CH₃ group at one end and a polar carboxylic acid COOH group at the other. The latter group confers water solubility while the hydrocarbon chain prevents it. It is the balance between these two forces that provides the monolayer forming abilities of the n-octadecanoic acid. If the hydrocarbon chain were too short, or the polar group too strong, then the material would simply dissolve in the subphase.

2.3 Monolayer stability

Most monolayer materials are applied to the subphase surface by first dissolving them in a suitable solvent (e.g., chloroform). When the solvent has evaporated, the organic molecules may be compressed to form a floating 'two-dimensional' solid. The hydrophilic and hydrophobic ends of the molecules ensure that, during this process, the individual molecules are aligned in the same way.

When the material is first applied to the surface of water, spreading will continue until the surface pressure has risen to an equilibrium value. This *equilibrium spreading pressure* is defined as that spontaneously generated when the bulk solid is placed in contact with a water surface (Iwahashi et al., 1985). Again, a comparison may be drawn with the vapour pressure of a bulk solid. An equilibrium vapour pressure exists for the solid in the presence of its vapour. If this vapour pressure is exceeded, i.e., the vapour

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becomes *supersaturated*, deposition onto the solid surface will occur. This should also be the case for a monolayer, which is expected to form crystals if its surface pressure is greater than the equilibrium spreading pressure. The formation of small droplets or lenses is often observed when excess monolayer material is spread. However, in many experiments, seemingly stable surface pressures up to higher values than the equilibrium spreading pressure may be measured. Deposition from such compressed layers may be compared to nucleation from supercooled or supersaturated bulk states.

The solubility of n-octadecanoic acid in water at 20 °C is approximately 290 µg per 100 ml. In a typical monolayer experiment, a few tens of µg of the compound might be spread on the surface of several hundred ml of water. The resulting compressed monolayer film is stable (if the surface pressure is not too high) over a long period. There is a barrier to dissolution and equilibrium may be approached only very slowly. Consequently, *a floating monomolecular film may be in a metastable state rather than in true thermodynamic equilibrium.*

2.4 Monolayer phases

As the monolayer is compressed on the water surface, it will undergo several phase transformations. These are, almost, analogous to the three-dimensional gases, liquids and solids described in chapter 1. The phase changes may be readily identified by monitoring the surface pressure Π as a function of the area occupied by the film. This is the two-dimensional equivalent of the pressure versus volume isotherm for a gas/liquid/solid (see figure 1.6). Figure 2.4 shows such a plot for a hypothetical long chain organic monolayer material (e.g., a long-chain fatty acid). This diagram is not meant to represent that observed for any particular substance, but shows most of the features observed for long chain compounds (Gaines, 1966).

In such a plot, it is usual to divide the film area A by the total number of molecules on the water surface to obtain the *area per molecule*, a , i.e.

$$\text{area per molecule} \rightarrow a = \frac{\overset{\text{area}}{AM}}{\overset{\text{weight}}{cN_A V}} = \frac{A}{cN_A V} \quad (2.4)$$

where M is the molecular weight of the monolayer material, C is the concentration of the spreading solution in mass per unit volume, c is the specific molar concentration of the solution and V is its volume.

In the 'gaseous' state (G in figure 2.4), the molecules are far enough apart on the water surface that they exert little force on one another. As the surface area of the monolayer is reduced, the hydrocarbon chains will begin to interact. The 'liquid' state that is formed is generally called the *expanded* monolayer phase (E). The hydrocarbon chains of the molecules in such a

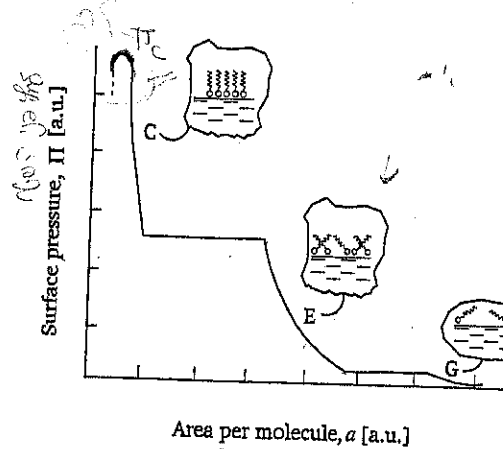


Figure 2.4 Surface pressure versus area per molecule isotherm for a long-chain organic compound. (The surface pressure and area are in arbitrary units, [a.u.])

film are in a random, rather than a regular orientation, with their polar groups in contact with the subphase. As the molecular area is progressively reduced, condensed (C) phases may appear. There may be more than one of these and the emergence of each condensed phase can be accompanied by constant pressure regions of the isotherm, as observed in the cases of a gas condensing to a liquid and a liquid solidifying (cf. figure 1.6). These regions will be associated with enthalpy changes in the monolayer. In the condensed monolayer states, the molecules are closely packed and are oriented with the hydrocarbon chain pointing away from the water surface. The area per molecule in such a state will be similar to the cross-sectional area of the hydrocarbon chain, i.e., $\approx 0.19 \text{ nm}^2 \text{ molecule}^{-1}$.

It is found that monolayers can be compressed to pressures considerably higher than the equilibrium spreading pressure. The surface pressure continues to increase with decreasing surface area until a point is reached where it is not possible to increase the pressure any further and the area of the film decreases if the pressure is kept constant, or the pressure falls if the film is held at constant area. This is referred to as *collapse*. The forces acting on a monolayer at this point are quite high. For example, a surface pressure of 100 mN m^{-1} acting on a layer of molecules 2.5 nm high corresponds to a three-dimensional pressure of about 400 atmospheres. The onset of collapse depends on many factors, including the rate at which the monolayer is being compressed and the history of the film. Therefore, to be meaningful, the pressure value should specify the exact conditions for collapse. When collapse occurs, molecules are forced out of the monolayer, as illustrated in figure 2.5.

Other structures are also possible for amphiphilic molecules. For example, if the molecules possess a strong polar head group relative to the nonpolar part

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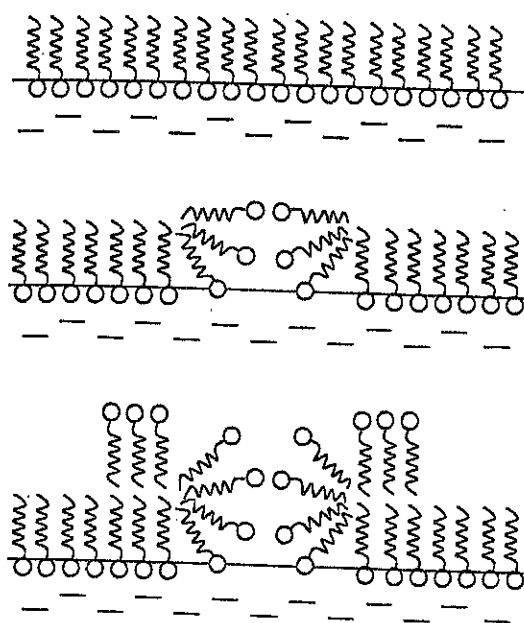
collapse
monolayer

Figure 2.5 Stages of collapse of a monolayer, going from the top to the bottom diagram.

of the molecule, *micelles* are formed if the concentration of the amphiphilic material is above a certain value (*critical micelle concentration*) (Harkins, 1952). In this arrangement, the molecules are arranged in spheres, with the polar head groups on the outside and the hydrocarbon chains towards the centre. If the head group of the amphiphilic molecule is not strong compared with the hydrophobic part, the molecules can form spherical *vesicles* in which the double layers form a shell with water both outside and inside. Such structures are very common in the biological world with long-chain molecules that possess two hydrocarbon chains for each polar head group (phospholipids). Schematic diagrams of both micelles and vesicles are shown in figure 2.6.

2.4.1 Gaseous phase

If the behaviour of gaseous monolayers can be modelled using a two-dimensional variation of conventional kinetic theory, then the molecules in the film may be assumed to move about with an average translational kinetic energy of $kT/2$ for each degree of freedom. This leads to the following 'ideal' gaseous monolayer equation (cf. equation (1.2) for a perfect three-dimensional gas)

$$\Pi a = kT \quad (2.5)$$

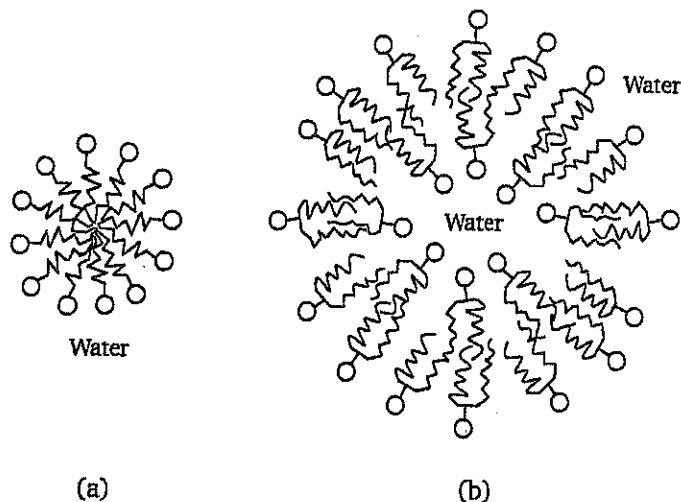


Figure 2.6 Cross sections of (a) a micelle and (b) a vesicle formed by amphiphilic molecules.

If Π is measured in $[\text{mN m}^{-1}]$ and a is in $[\text{nm}^2 \text{ molecule}^{-1}]$, their product should be 3.97 at 15°C . Therefore, the surface pressure in the gaseous phase would be expected to be about 1 mN m^{-1} at an area per molecule of 4 nm^2 . This is consistent with experimental data for various long-chain molecules (Harkins, 1952). As a gaseous monolayer is compressed on the subphase surface, the expanded (liquid-like) state will normally appear. Usually, this is accompanied by a constant pressure region in the isotherm, in which the floating film consists of a mixture of two phases. The phase change is generally thought of as a first-order thermodynamic transition, analogous to evaporation in three dimensions. Some workers have postulated the existence of monolayers in which there is a gradual transition between the gaseous and expanded states (Harkins, 1952; Gaines, 1966). This may be similar to the compression of a three-dimensional gas above its critical temperature, as shown in figure 1.6 (isotherm at temperature T_3).

2.4.2 Expanded phase

The nature of the expanded and condensed phases formed on compression of a gaseous monolayer may be more conveniently discussed by reference to the pressure versus area isotherms for specific materials. Figure 2.7 shows such a plot for *n*-pentadecanoic acid ($\text{C}_{14}\text{H}_{29}\text{COOH}$), measured at 25°C and on a subphase of 10^{-2} M HCl (Pallas and Pethica, 1985). The expanded phase (E) is evident at surface pressures below 6 mN m^{-1} (the gaseous phase was not observed in this experiment). The area per molecule in the expanded monolayer is much less than that expected for gaseous monolayers (equation

Figure 2.7
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2.5), but in a cross section of the expanded phase the surface pressure and the area per molecule are constant. A plateau at the appearance of the expanded phase is characteristic of a first-order transition. It has been some decades since the first chain organic monolayers were expanded to condensed states. Many transitions have been reported (Pethica, 1985). The expanded phase is considerably less dense than the condensed phase. The expanded phase is a liquid-like phase and the temperature dependence of the isotherms for $\text{C}_{15}\text{H}_{31}\text{COOH}$ and Pethica, 1985) is a decrease in the

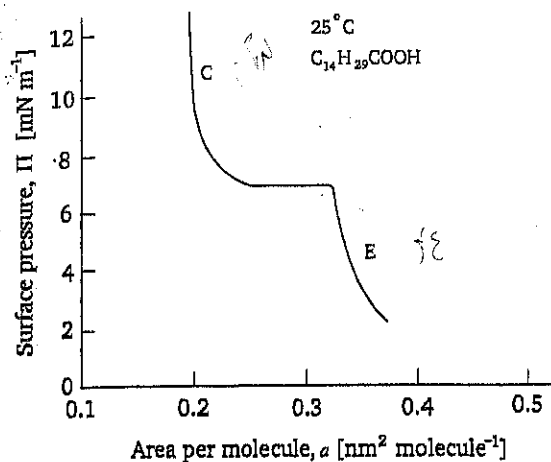


Figure 2.7 Surface pressure versus area per molecule isotherm for *n*-pentadecanoic acid, at 25°C on a subphase of 10^{-2} M HCl. (Reprinted with permission from Pallas, N. R. and Pethica, B. A. (1985) *Langmuir*, 1, 509-13. Copyright 1985 American Chemical Society.)

2.5), but is still significantly greater than the area associated with the cross-section of the cylindrically shaped fatty acid molecule ($\approx 0.19 \text{ nm}^2$). In the expanded phase, the area per molecule varies considerably with the surface pressure and there is no apparent relation between the observed molecular area and the dimensions of the constituent molecules.

A plateau at a surface pressure of about 7 mN m^{-1} in figure 2.7 indicates the appearance of a condensed (C) monolayer phase. The constant pressure region is characteristic of a first-order thermodynamic transition. There has, however, been some debate on this point. For example, many isotherms for simple long-chain organic compounds do not show (completely) horizontal sections for the expanded to condensed transition. This has led to speculation that higher-order transitions may be involved. However, it is probably more likely that constant Π regions are not observed because of the effect of impurities (Pallas and Pethica, 1985). The finite number of molecules involved in monolayer phase transitions (compared to three-dimensional phase transitions) can also considerably shorten the constant pressure plateau (Birdi, 1989).

The expanded to condensed phase changes observed in simple long-chain compounds are affected markedly by the length of the hydrocarbon chain and the temperature. This is illustrated by figure 2.8, which shows the isotherms for *n*-pentadecanoic acid and *n*-hexadecanoic acid (palmitic acid - $\text{C}_{15}\text{H}_{31}\text{COOH}$) measured at 30°C and on a subphase of 10^{-2} M HCl (Pallas and Pethica, 1985). Comparison with figure 2.7 reveals that an increase in temperature has increased the surface pressure of the phase transition. A decrease in the hydrocarbon chain length produces a similar result. Both

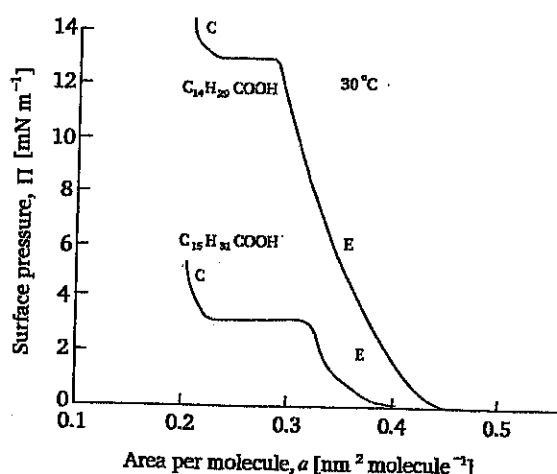


Figure 2.8 Surface pressure versus area per molecule isotherms for *n*-pentadecanoic acid and *n*-hexadecanoic acid, at 30°C on a subphase of 10^{-2} M HCl. (Reprinted with permission from Pallas, N. R. and Pethica, B. A. (1985) *Langmuir*, 1, 509-13. Copyright 1985 American Chemical Society.)

effects may be understood by considering the forces between the molecules in the floating monolayer. A decrease in the length of the chain leads to decreased van der Waals' forces between the molecules, resulting in reduced cohesion within the film (with a consequent reduction in the melting point of the bulk material); in contrast, a decrease in temperature leads to less thermal motion, tending to condense the film. As a rule, reducing the hydrocarbon chain length of a long-chain fatty acid by one methylene group is roughly equivalent to a temperature increase of 5-10 K. The isotherms in figures 2.7 and 2.8 should also be contrasted with those shown in figure 1.6 for a three-dimensional substance. Further reductions in temperature (or increases in chain length) are expected to result eventually in the disappearance of the expanded to condensed phase change as the gaseous monolayer condenses directly to a solid.

There have been several attempts to develop theoretical models for two-dimensional phase transitions, such as that from an expanded to a condensed monolayer state. If it is assumed that van der Waals' forces between the hydrocarbon chains are largely responsible for the transitions in long-chain fatty acids, then the following expression may be written for the internal energy of the molecules (Jähnig, 1979; Marcelja, 1974)

$$U = E_{\text{intra}} + E_{\text{disp}} + \Pi a \quad (2.6)$$

where E_{intra} is the internal energy of a single chain in a given conformation and E_{disp} gives the van der Waals' interaction of the chain with its neighbours

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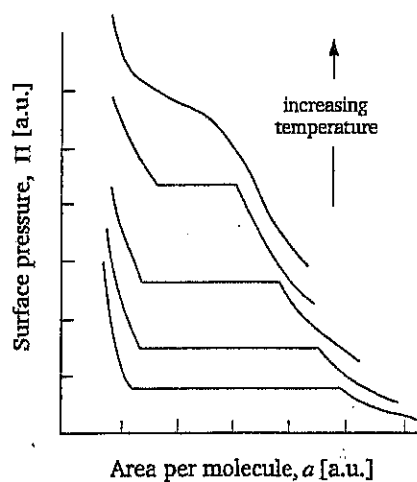


Figure 2.9 Theoretical surface pressure versus area per molecule isotherms for a long-chain molecule at different temperature. (After Marcelja, 1974. Reproduced with permission from Elsevier Science.)

(this force of attraction results from an electron correlation effect and is also called the *London force* or *dispersion force* (Tredgold, 1994)). On this basis, a series of theoretical surface pressure versus area isotherms may be generated (Marcelja, 1974). As shown in figure 2.9, these curves do show qualitative agreement with experimental data (figures 2.7 and 2.8). Modelling of monolayers is further discussed in the book by Ulman (1991).

The coexistence of both condensed and expanded phases in floating monolayers may be observed directly by incorporating a small fluorescent dye probe into the film. Figure 2.10 gives the results of such an experiment using a particular phospholipid (Lösche et al., 1988). The photographs were taken at the points shown on the pressure versus area curve and reveal the existence of two phases as the monolayer is compressed in the constant pressure region of the isotherm. Nuclei of the condensed phase appear when the plateau in the isotherm is reached (photograph a). These domains are compact and their mean size increases with increasing surface pressure. Finally, a hexagonal lattice is formed (photograph g).

An alternative observation method is *Brewster angle microscopy* (section 7.6). Figure 2.11 shows micrographs of the expanded to condensed phase transitions observed by this technique for fatty acid and phospholipid monolayers (Hönig and Möbius, 1992). While the fatty acid (photograph (a)) shows large circular domains, the phospholipid domains (photograph (b)) exhibit more complex shapes. Such images may be analysed to obtain information concerning molecular orientation (Overbeck et al., 1994a & b).

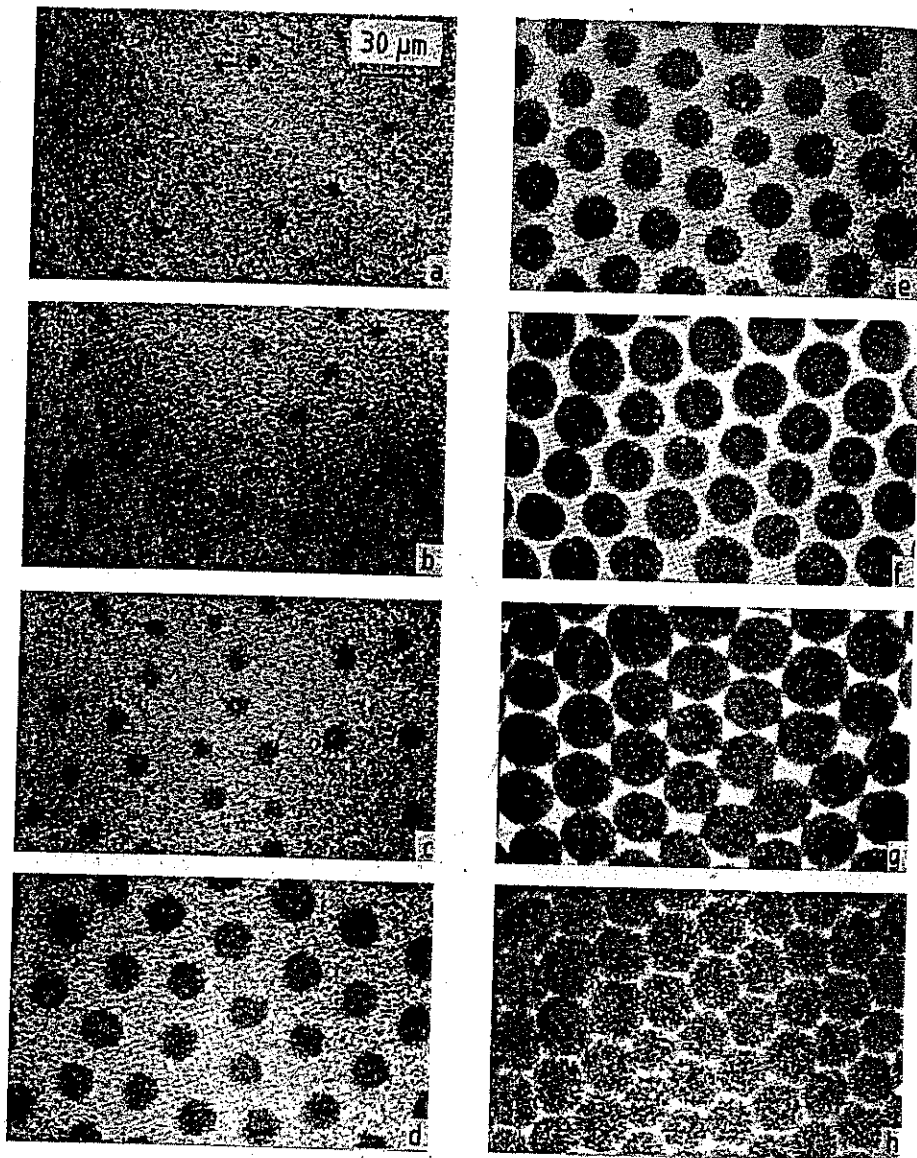


Figure 2.10 Fluorescence micrographs of a phospholipid monolayer (dimyristol-phosphatidic acid), doped with a dye, at different points on the isotherm as indicated opposite. (After Lösche et al., 1988. Reproduced with permission from Academic Press.)

2.4.3 Condensed phases

As the length of the hydrocarbon chain in a simple long-chain fatty acid is increased, the expanded state disappears and a direct transition from a gas

to a condensed phase of *n*-docosanoic acid at 15 °C and (Lipschitz et al., 1955). Two liquid phases are identified by very

The nomenclature is confusing (Goulet and Goulet, 1955). The condensed phase is liquid, S (solid), for some of the phases that the phase is condensed phase. X-ray diffraction

An inspection of the molecule (see Fig. 2.10) shows the molecule in various monolayers at different arrangements. The lower pressure is compressible. The normal to the surface is towards the next nearest neighbor (Lipschitz et al., 1992a).

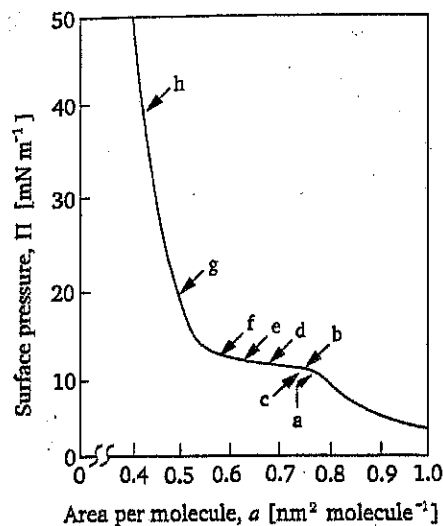


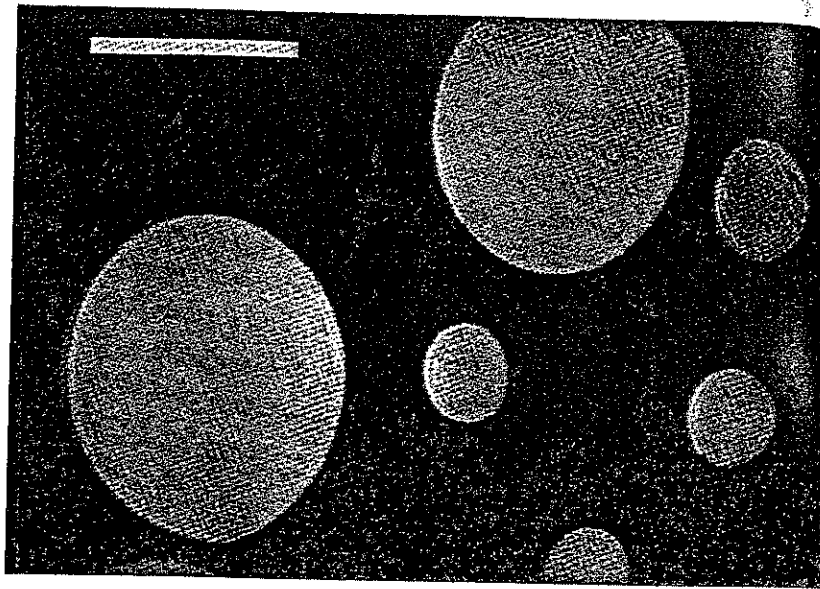
Figure 2.10 (cont.)

to a condensed phase takes place. This is illustrated by the isotherm for *n*-docosanoic acid (behenic acid – $C_{21}H_{43}COOH$), recorded at a temperature of $15^\circ C$ and on a subphase of $0.01 NH_4Cl$, shown in figure 2.12 (Stenhagen, 1955). Two low-pressure phases and two high pressure phases may be identified by very careful measurement.

The nomenclature used by various workers to describe these phases can be confusing (Gaines, 1966). Here, the method adopted by Harkins (1952) is used. The condensed phases include L_2 , L'_2 (liquid condensed), LS (superliquid), S (solid) and CS (close-packed solid). *The use of the term 'liquid' for some of these monolayer states simply reflects the historical assumptions that the phases were liquid-like.* However, it is now known that all the condensed phases have well-defined in-plane structures and exhibit distinct X-ray diffraction peaks (Dutta, 1990).

An inspection of the abscissa in figure 2.12 reveals that the area per molecule of the various condensed monolayer phases is approaching that of the molecular cross-section. It is therefore reasonable to assume that the various monolayer states are related to different interactions, and therefore different arrangements, of the polar groups and hydrocarbon chains. Both the lower pressure L_2 and L'_2 phases observed in figure 2.12 are fairly compressible. These phases have the long axes of the molecules tilted from the normal to the interface plane: in the L_2 phase, the alkyl chains are tilted towards the nearest neighbours and the L'_2 state has chains tilted towards the next nearest neighbours (90° away from the L_2 tilt direction) (Shih et al., 1992a).

(a)



(b)

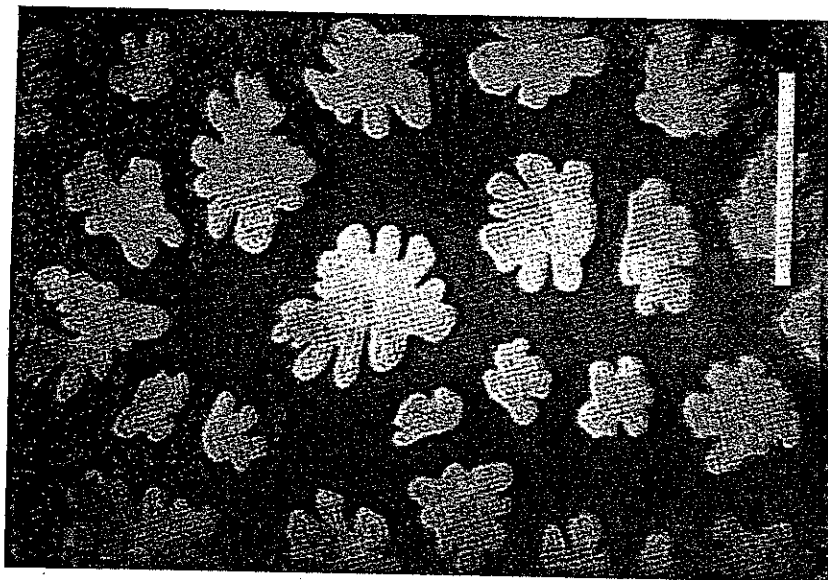


Figure 2.11 Brewster angle micrograph of the expanded to condensed phase transition in: (a) pentadecanoic acid (surface pressure $\approx 5 \text{ mN m}^{-1}$); (b) a phospholipid (dimyristoyl-phosphatidylethanolamine) (8 mN m^{-1}). Subphase temperature $\approx 22^\circ\text{C}$. The bars on the photographs correspond to $100 \mu\text{m}$. (Photographs provided by Dirk Hönig and Daniela Spohn, Max-Planck-Institut für biophysikalische Chemie, Göttingen, Germany.)

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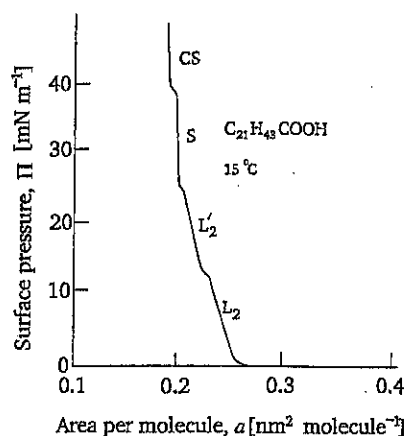


Figure 2.12 Surface pressure versus area per molecule isotherm for *n*-docosanoic acid, at 15 °C on a subphase of 10⁻² N HCl. (After Stenhagen, 1955. Reproduced with permission from Academic Press.)

When a surface pressure of about 25 mN m⁻¹ is reached, the floating monolayer becomes comparatively incompressible and the S phase is apparent. Further compression leads to the CS state, which eventually collapses with increasing surface pressure. The various transitions between the condensed monolayer phases are often accompanied by a (very) short region of constant pressure, possibly associated with the enthalpy change of a first order transition. For the higher pressure phases, the chain axes are normal to the interface plane.

The LS phase is characterized by a very low viscosity over a certain temperature range (Harkins, 1952). It has also been called a *rotator* phase, after the corresponding structures in lamellar paraffins (Shih et al., 1992a). This monolayer state is not observed in the isotherm in figure 2.12.

The precise nature and the molecular arrangement of the various condensed monolayer phases have been the subject of considerable speculation (Stenhagen, 1955; Gaines, 1966). It is now becoming evident that the various monolayer states are similar to mesophases found in the smectic liquid crystals described in chapter 1 (Peterson, 1992). For example, X-ray diffraction of floating fatty acid monolayers has revealed that phases L₂ and L'₂ show the same unit cell symmetries as the smectic liquid crystalline phases S_I and S_F, respectively (Kenn et al. 1991). Details of these mesophases may be found in the book by Gray and Goodby (1984). Table 2.1 provides a summary of the main condensed monolayer phases that have been observed with long-chain compounds, with some of their characteristics. Transitions L'₂ → LS, LS → S, S → CS, L'₂ → CS and L₂ → CS involve discontinuities in density, as expected in first-order thermodynamic phase changes.

It should be noted that monolayer states other than those listed in table 2.2 may exist. For example, smectic S_H and S_K phases have been identified

Table 2.2 Condensed monolayer phases for long-chain organic compounds and their corresponding smectic liquid crystalline phases. (After Kenn et al., 1991.)

Phase	Name	Smectic LC phase	Characteristics
L_2	liquid-condensed	S_I	tilted molecules
L'_2	liquid-condensed	S_F	tilted molecules, but with tilt direction at 90° to L_2 phase; similar compressibility to L_2 phase.
LS	super-liquid	hexatic S_B	low viscosity at certain temperatures; upright molecules; less compressible than L_2 and L'_2 phases; similar compressibility to S and CS phases.
S	solid	S_E	upright molecules; high collapse pressure.
CS	close-packed solid	polycrystalline solid	upright molecules; high collapse pressure; lower collapse area than S phase.

for n-docosanoic acid (Bibo and Peterson, 1992). A further phase, the hexatic smectic-L appears when the n-docosanoic acid is mixed with ethyl eicosanoate. This phase is predicted to occur between the smectic S_I and S_F phases (see section 1.2).

2.4.4 Phase diagrams

If the surface pressure versus area measurements are undertaken at several temperatures, and the points corresponding to the same phase transitions are plotted on a pressure versus temperatures diagram, the resulting diagram will show the range of temperature and pressures over which the various phases exist. Such a phase diagram for n-docosanoic acid is given in figure 2.13. It is now evident why the LS phase is not observed in the isotherm shown in figure 2.12. A vertical line corresponding to 15°C will pass through the phases L_2 , L'_2 , S and CS. However, the LS phase will not appear in the pressure versus area diagram unless the temperature is increased to about 25°C . It should be emphasised that the phase diagram shown in figure 2.13 is probably an oversimplification; a generalized diagram for long-chain fatty acids is given by Overbeck et al. (1994b).

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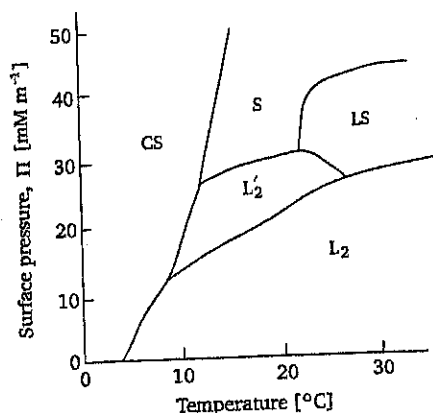


Figure 2.13 Surface pressure versus temperature phase diagram for n-docosanoic acid. (After Peterson, 1992. Reproduced with permission from Research Studies Press.)

The nature of phase diagrams for monolayer-forming materials has very important implications for the control of variables such as temperature and surface pressure in monolayer experiments (and for the transfer of monolayers to solid supports). For instance, if a monolayer is controlled so that it is in a condensed phase that is very close to a phase boundary in the phase diagram, a small change in either temperature or surface pressure may alter the state of the floating layer, affecting the deposition characteristics of the monolayer on solid supports.

The monolayer characteristics of many organic materials may be found in the comprehensive handbook edited by Mingotaud et al. (1993).

2.4.5 Surface phase rule

Gibbs' phase rule, introduced in chapter 1, may be extended to monolayer phases in equilibrium (Birdi, 1989; Gaines, 1966). Here the relationship is written

$$F = (C^b + C^s) - (P^b + P^s) + 3 \quad (2.7)$$

where C^b is the number of components in the bulk, C^s is the number confined to the surface, P^b is the number of bulk phases and P^s is the number of surface phases in equilibrium with each other. For a monocomponent monolayer at the interface between a pure liquid and a pure gas

$$C^b = 2; \quad C^s = 1; \quad P^b = 2; \quad P^s = 1.$$

There are three degrees of freedom. If the temperature and external pressure are fixed (as in most monolayer experiments), then there is only one independent variable. Consequently, the surface pressure will vary

with the area of the monolayer. If there are two phases present in the monolayer (e.g., expanded and condensed), then there are only two degrees of freedom. Normally, the external pressure and temperature are already fixed. The surface pressure must therefore remain constant during the phase transformation, as shown in the isotherms in figures 2.7 and 2.8. For three surface phases to be in equilibrium simultaneously, there are no additional degrees of freedom. This is evident from the phase diagram in figure 2.13, e.g., the areas corresponding to the L_2 , L'_2 and LS phases meet at a point of defined temperature and surface pressure. The application of the phase rule to multicomponent systems is discussed in section 2.7.

2.5 Monolayer compressibility and viscosity

An important characteristic of a monolayer phase is its *compressibility* C . By analogy with the compressibility for a bulk material, this is defined

$$C = -\frac{1}{a} \left(\frac{\partial a}{\partial \Pi} \right)_{T, P, n_i} \quad (2.8)$$

where n is the number of moles of material. Therefore C may be evaluated directly from the slope of the surface pressure versus area isotherm. Figure 2.12 shows that the compressibility of the lower pressure L_2 and L'_2 phases of *n*-docosanoic acid is about an order of magnitude greater than that for the more condensed S and CS phases. For the L_2 and CS phases, these values are approximately $8 \times 10^{-3} \text{ m mN}^{-1}$ and $3 \times 10^{-4} \text{ m mN}^{-1}$, respectively (Kenn et al., 1991).

A comparison can also be made between the rheological properties of monolayer films and those of bulk matter. If the monolayer is highly rigid, it will act in a similar way to a solid when a stress is applied and deform elastically. It may be appropriate to describe this kind of behaviour using a set of elastic moduli (Gaines, 1966). In contrast, some phases of floating monolayers may be more similar to liquids and the layer will flow in response to an applied shear stress. A useful parameter to quantify this behaviour is the *coefficient of surface viscosity* η_s given by

$$(\text{shear stress}) = \eta_s \times (\text{rate of flow}) \quad (2.9)$$

The shear stress in the monolayer is simply the tangential force per unit length. The surface viscosity may be independent of shear rate (Newtonian behaviour), or may change with the rate of flow (non-Newtonian). Sometimes complex viscoelastic behaviour can result in surface pressure variations across the monolayer and consequently to compression rate dependent hysteresis in a compression-expansion isotherm measurement. In such cases it is

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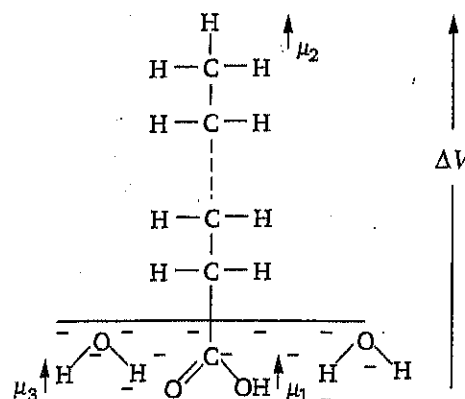


Figure 2.14 Origin of the surface potential ΔV in a long-chain fatty acid molecule at the air/water interface.

important that the nature of the compression mechanism (e.g., uniaxial, isotropic) and the compression rate are stated with the pressure versus area curve. There may also be implications for the transfer of the monolayer onto a solid support; this is discussed further in the next chapter.

2.6 Electrical effects in monolayers

Measurement of the electrical properties of the monolayer/air interface can also provide some insight into the nature of the various phases and phase changes. A convenient experimental technique is to monitor the *surface potential* ΔV . This is the potential difference produced at a point immediately above the subphase surface when a floating monolayer is introduced. It arises because monolayer-forming materials usually possess permanent electric dipoles. If the floating film is thought of as an array of dipoles whose effective dipole moments in the direction perpendicular to the subphase surface are μ_{\perp} , the surface potential may be approximated by

$$\Delta V = \frac{n\mu_{\perp}}{\epsilon_0} \quad (2.10)$$

where n is the surface density of dipoles (i.e., the number of molecules per unit area) and ϵ_0 is the permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$). The choice of a relative permittivity of unity in equation (2.10) is arbitrary and better agreement with experimental data can be obtained by introducing an effective local permittivity (Oliveira et al., 1992). The overall dipole moment μ_{\perp} will include contributions from the polar head group of the molecule (μ_1), the hydrocarbon chain (μ_2) (associated with the CH_3 group at the end of the molecule) and the surface water molecules (μ_3), as shown in figure 2.14. For a fully condensed monolayer of n-octadecanoic acid,

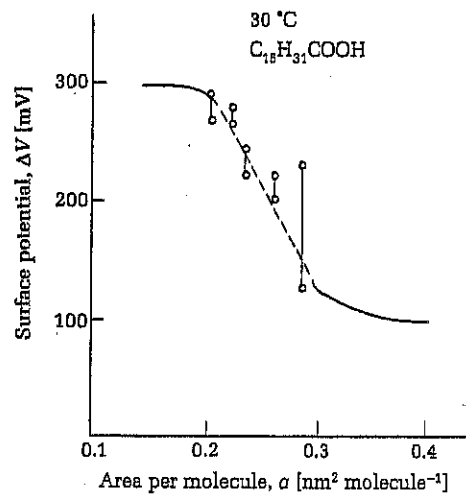


Figure 2.15 Surface potential versus area per molecule plot for *n*-hexadecanoic acid, at 30 °C on a subphase of 10^{-2} M HCl. (Reprinted with permission from Pallas, N. R. and Pethica, B. A. (1985) *Langmuir*, 1, 509–13. Copyright 1985 American Chemical Society.)

$\mu_1 = 990$ mD, $\mu_2 = 330$ mD and $\mu_3 = -65$ mD (Oliveira et al., 1992). If the monolayer becomes ionized (see below), then it is necessary to include the potential due to the double-layer (see next section).

As a monolayer of *n*-octadecanoic acid is compressed, the surface potential will remain close to zero until the average area per molecule is less than 0.4 nm^2 (Oliveira et al., 1992). A rapid increase in ΔV then occurs until a maximum value of several hundred millivolts is achieved. Large fluctuations in ΔV can occur for monolayers in a two phase region. These potential variations reflect the presence of patches of dense and dilute monolayer, observable by the finite size of the measuring electrode. An example is shown in figure 2.15 for *n*-hexadecanoic acid on 10^{-2} M HCl at 30 °C (Pallas and Pethica, 1985). This curve should be contrasted with the pressure versus area curve, measured under identical conditions, shown in figure 2.8.

It is also possible to monitor the *displacement current* generated as the dipoles in the monolayer re-organize during compression (Iwamoto et al., 1992). The technique is similar to that of *thermally stimulated conductivity* (or *thermally stimulated depolarization*) of a dielectric (Harrop, 1972; Blythe, 1979). However, in the latter case, the dipole re-orientation is caused by a temperature change (see section 6.6.4).

2.6.1 Ionized monolayers

The discussion so far has been confined to monolayers of neutral molecules that bear no electrical charge. This would be the situation for a long-chain

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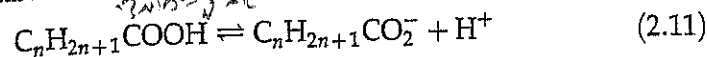
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fatty acid at a pH of 4 or less. However, on making the subphase more alkaline, ionization of the polar head groups will occur to form hydrogen ions in the subphase and carboxylate ions in the film, i.e.,



The pH at which half the molecules of an acid are ionized is known as the pK_A of the acid. The expected pK_A for n-octadecanoic acid on a water surface is 5.6 (Betts and Pethica, 1956). Charges associated with ionized monolayers will be neutralized by counterions in (or added to) the aqueous subphase. The distance over which this neutralization or 'screening' occurs is related to the concentration of these ions. The resulting electric potential will modify the measured surface potential. To a first approximation, this will now be given by

$$\Delta V = n\mu_{\perp} + \psi_0 \quad (2.12)$$

where ψ_0 represents the maximum potential difference between the surface and the bulk of the subphase.

The exact form of the variation of the potential ψ with distance beneath the floating monolayer is complex; for example, it is likely that ψ_0 will depend on μ_{\perp} (Gaines, 1966). A simplified model, based on the classic Gouy-Chapman theory, is shown in figure 2.16 (Birdi, 1989). It is assumed that the monolayer is negatively charged at the air/water interface ($x = 0$ in the figure). Positively and negatively charged ions in the subphase will then be distributed to achieve charge neutrality. This distribution will be governed by Boltzmann statistics, resulting in a variation of ψ from a maximum value of ψ_0 at the surface to zero in the bulk of the subphase. The distance over which ψ changes is known as the diffuse or Gouy-Chapman double layer ($x = 0$ to $x = L$ in figure 2.16). In the real situation specific ions may be adsorbed on the polar ends of the monolayer or may even penetrate this layer; furthermore ions in solution are likely to be solvated (surrounded by oriented water molecules) and can approach the surface only to a distance about equal to the radius of the solvated ions.

One important consequence of the above is that the pH of the surface region will differ from that of the bulk (Gaines, 1966)

$$\text{pH}_s = \text{pH}_b + \left(\frac{q\psi}{2.3kT} \right) \quad (2.13)$$

where pH_s is the surface pH, pH_b is that of the bulk solution, and q is the electronic charge (1.60×10^{-19} C).

Langmuir-Blodgett films of long-chain fatty acids are often prepared by deliberately adding divalent ions to the subphase to improve the deposition characteristics of the monolayer film. The floating layer will be a mixture of the fatty acid and the fatty acid salt. The salt concentration in the

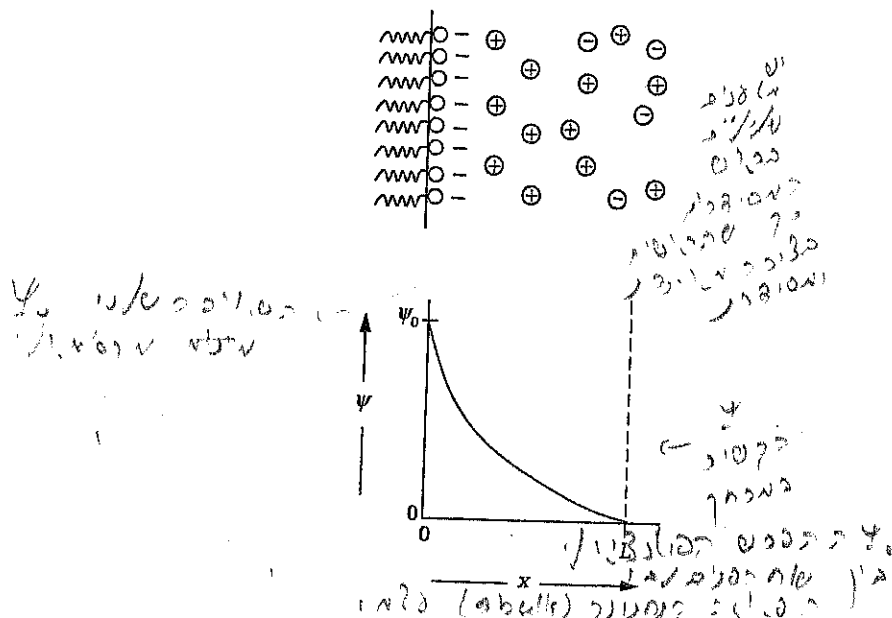
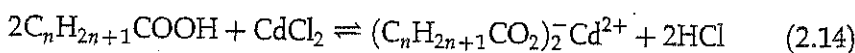


Figure 2.16 Top: simple model for the charge distribution at an air/monolayer/water interface. Bottom: variation of potential ψ with distance.

monolayer will depend upon the pH. In a subphase containing cadmium chloride, the following reaction will take place



The salt formation is favoured by high subphase pH. In the specific case of a floating monolayer of n-eicosanoic acid (arachidic acid) on a subphase at room temperature containing a cadmium salt in a concentration of 10^{-4} M and having a pH = 5.7, a monolayer comprising about 50% cadmium eicosenoate and 50% eicosanoic acid will be formed (Blodgett and Langmuir, 1937).

Figure 2.17 shows the effect of the incorporation of calcium ions on the pressure versus area isotherms for n-heneicosanoic acid (Shih et al., 1992b). The isotherms have been displaced horizontally for clarity. At the lowest pH (2.1), the isotherm is identical to that observed at the same temperature without ions in the subphase. The L_2 and L_2' phases, together with the transition to a condensed monolayer state, are evident. However, as the pH is increased, the structure in the isotherms corresponding to the phase transitions is lost. At the highest pH (10.4), the surface pressure versus area curve for the salt monolayer is featureless. The general forms of the isotherms in figure 2.17 are observed for many long-chain fatty acid/salt combinations. The formation of the salt monolayer appears to convert the floating monolayer into a more condensed solid as the head groups are drawn closer together and the tails move closer to the vertical (Shih et al., 1992b). Theoretical studies

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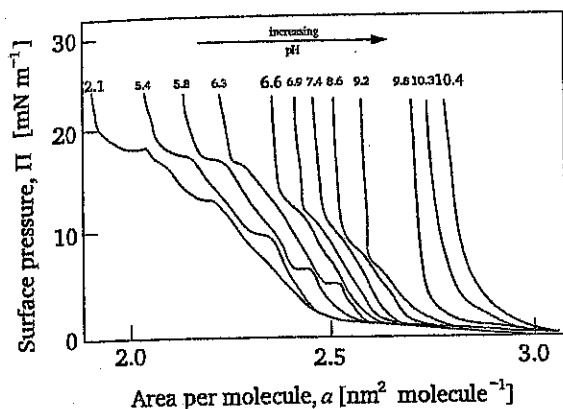


Figure 2.17 Pressure versus area per molecule isotherms, at different pH values, for monolayers of *n*-heneicosanoic acid spread on a solution of 0.5 mN calcium chloride. The isotherms have been displaced horizontally for clarity; the abscissa is valid only for the isotherm at pH 2.1. (After Shih et al., 1992b. Reproduced with permission from the American Institute of Physics.)

also show that the role of ions in fatty acid monolayers is to provide long-range attractive forces that cause a two-dimensional lattice to form, even at low amphiphile concentrations (Modak and Datta, 1994).

Addition of ions to the subphase can also affect the mechanical properties of the surface monolayer. Traces of triply charged cations in particular (e.g., Fe^{3+} , Al^{3+}) can give rise to extremely rigid layers (Hann, 1990).

2.7 Mixed monolayers

Interest in molecular electronics and molecular engineering has led to many studies of mixed monolayer systems. Sometimes a fatty acid is simply used to 'stabilize' a compound that would not form a monolayer by itself. The resulting layers could be intimate mixtures, as shown in figure 2.18(a), or a multiphase mixture (figure 2.18(b)). The precise arrangement may usually be identified by studying an appropriate monolayer property (e.g., collapse pressure or compressibility) over a wide composition range. If the individual components are immiscible, then the film may be thought of as consisting of two (or more) separate monolayers. The area occupied by the film will be the sum of the areas of the separate films, i.e., for a two-component mixture

$$a_{12} = x_1 a_1 + x_2 a_2 \quad (2.15)$$

where a_{12} is the average molecular area in the two-component film, x_1 and x_2 are the mole fractions of the components, and a_1 and a_2 are the molecular

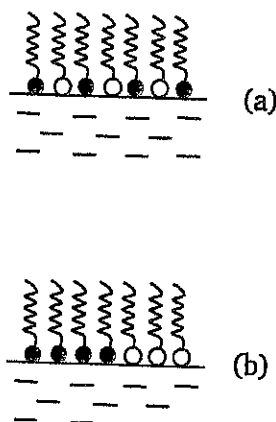


Figure 2.18 Different arrangements for the molecules in a two-component monolayer: (a) complete miscibility; (b) immiscible materials.

areas in the two single component films at the same surface pressure. For an 'ideal' mixed film, a plot of a_{12} versus x_1 should be a straight line. Any deviation from this relationship provides evidence for miscibility. Similar scaling rules may be used for other properties such as surface potential and compressibility.

Using the surface phase rule (equation (2.7)) for two components in the monolayer

$$F = 5 - P^s \quad (2.16)$$

If there is only one surface phase (i.e., the two components are completely miscible), there are four degrees of freedom: temperature, the external pressure, the monolayer surface pressure and the composition of the film. However, if the monolayer components do not mix, two surface phases are formed and one degree of freedom is removed.

If the mixed monolayer is compressed until it collapses, an additional bulk phase will be formed as monolayer material is squeezed out of the floating layer (i.e., $P^b = 3$). Now

$$F = 4 - P^s \quad (2.17)$$

For one surface phase, there are three degrees of freedom, and if external pressure and temperature are constant, the surface pressure must vary with the composition. This surface pressure will be the equilibrium spreading pressure of the mixed film (i.e., the pressure at which the monolayer is in equilibrium with the bulk phase). In the case where the monolayer components are immiscible there are two surface phases ($P^s = 2$) and only two degrees of freedom. At a fixed temperature and external pressure, the equilibrium spreading pressure will be constant, independent of composition.

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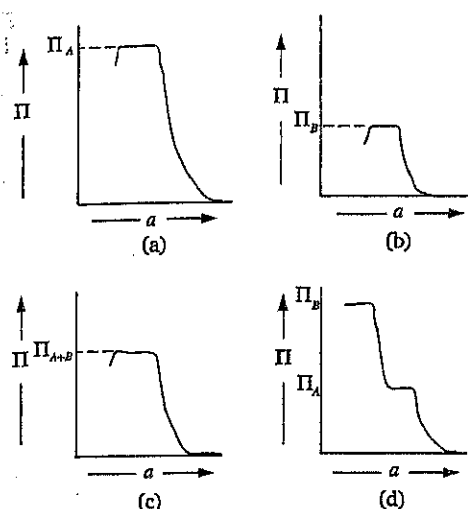


Figure 2.19 Surface pressure versus area per molecule isotherms for: (a) compound A; (b) compound B; (c) mixed monolayer of A and B with complete miscibility; (d) mixed monolayer of A and B with no miscibility.

The component of the mixed film that has the lower equilibrium spreading pressure will be squeezed out of the monolayer at the same surface pressure, whatever the initial composition of the monolayer. A measurement of equilibrium spreading pressure as a function of monolayer composition should therefore be a good test for monolayer homogeneity (see figure 2.19). Very often the collapse pressure is taken as a guide to the equilibrium spreading pressure. However, the results will require careful interpretation as the monolayer film may not be in a state of true thermodynamic equilibrium when collapse occurs.

2.8 Chemistry in monolayers

Several kinds of chemical interaction can take place between the monolayer film and one (or both) of the adjacent bulk phases. These include the oxidation of C=C bonds, hydrolysis, photochemical reactions (e.g., *cis-trans* isomerism) and polymerization. These subjects have been discussed by Bubeck (1988) and Gaines (1966).

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