LECTURE TEXT

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Transfer phenomena and interactions of non-aqueous phase liquids in soil and groundwater

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Abstract

Non-aqueous phase liquids are water immiscible organic liquids that are widely encountered in the environment. Exemplar NAPLs include chlorinated hydrocarbon solvents, petroleum products, and waste products such as coal tar. Real-world NAPLs are usually multi-component solution mixtures, and many of the components in NAPLs pose a major challenge to soil, air, and water quality. The purpose of this manuscript is to examine the key physico-chemical properties of NAPLs and how these affect the behaviour of NAPLs in the sub-surface environment.

Keywords NAPL · Solubility · Surface tension · Contact angle · Vaporisation · Viscosity

Introduction

The term non-aqueous phase liquid (NAPL) is a generic term used to describe a class of organic liquid contaminants that are characterised by their immiscibility with water. An additional distinction is made on the basis of density. Those liquids with a density greater than that of water are referred to as dense NAPLs (DNAPLs) and those that are less dense than water are called light NAPLS (LNAPLs). They are of environmental concern, because although immiscible with water—mixtures of water and NAPL separate into two distinct phases—they are soluble in water, albeit to a very limited extent. Yet, in many cases, their solubility may be many orders of magnitude greater than safe drinking water limits. For example, the United States Environmental Protection Agency has set a maximum aqueous concentration level of $5\ \mu g\ L^{-1}$ for benzene; yet, the solubility of benzene in water is about $1.79\ g\ L^{-1}$ (an approximately 6 orders of magnitude difference). Many NAPLs are also volatile and thus pose an air pollution hazard, especially in indoor environments.

Typical examples of DNAPLs include chlorinated hydrocarbon solvents such as trichloroethene, coal tars, and polychlorinated biphenyl oils. Exemplar LNAPLs include petrol (gasoline), fuel oils, and solvents such as petroleum ether.

NAPLs are released into the environment either through inappropriate or careless use, storage in leaking containers, spillage, or inappropriate disposal. Indeed, disposal practices that were considered best practice in the past, such as disposal in waste pits or disposal to soil surfaces to encourage atmospheric dispersal by evaporation have in many cases given rise to present day long-term pollution problems.

Although NAPLs have seen widespread use for over a century, it has only been relatively recently that their importance, as soil and groundwater contaminants have been recognised. This lack of recognition by the industrial, regulatory, and research communities was partly due to the fact that the analytical methods and equipment required to detect low concentrations of organic compounds in groundwater were not widely available or used until relatively recently [1].

When an NAPL is discharged into the soil environment, it will tend to migrate vertically downwards towards the water table. NAPLs readily displace air in the unsaturated sub-surface—this is the sub-surface soil zone, where pore spaces either contain air or water. NAPLs, however, do not necessarily displace water. The size of the capillary forces generated at the NAPL/water interface is pivotal in determining this outcome.

On the trailing edge of a migrating NAPL body, droplets of NAPL are detached and fill single or several contiguous

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pore spaces. Capillary forces are responsible for the trapping of these droplets, which are commonly referred to as residuals.

Residuals in the unsaturated zone will slowly evaporate to produce a vapour-phase contamination problem. Typically, vapours migrate to the soil surface providing a range of problems, which can include noxious smells, explosion risks, and health hazards. Infiltrating rainwater will also dissolve NAPL components which are then, subsequently, leached into groundwater.

The rate of migration of the NAPL body is determined by its viscosity and density [2]. High densities coupled with low viscosities give rise to highly mobile NAPL bodies. Chlorinated hydrocarbon solvents fall into this category.

NAPL bodies of sufficient volume are able to reach the water table. The water table is located in the saturated zone—the sub-surface region, where all pore spaces are occupied by water. The water table is located at the elevation, where water pressure is equal to atmospheric pressure. DNAPLs that exert sufficient pressure can sink below the water table to form pools of potentially mobile DNAPL and trapped residuals. The slow dissolution of DNAPL components from pools and residuals into flowing groundwater constitutes a long-term source of groundwater contamination. Buoyancy forces prevent LNAPLs from sinking below the water table. As a consequence, they tend to accumulate and spread in a complex manner above the water table. However, LNAPL bodies of sufficient mass will depress the water table.

The fate of NAPLs released into the environment is thus determined primarily by the physico-chemical properties of the NAPL. These include:

- Surface tension, interfacial tension, and contact angle, which when combined provide the capillary force constraints on transport through a variably water saturated porous medium.
- Composition: NAPLs are rarely single component phases. Some components of NAPL bodies maybe important risk drivers (i.e., they are extremely hazardous to human or ecological health), whilst others may affect NAPL transport and fate. Composition is also important from the point of view of environmental forensics, since complex compositions act as environmental fingerprints which when interpreted correctly can provide clues as to the origin of NAPL sources.
- Solubility and vapour pressure determine the mass transfer of NAPL components to the aqueous and vapour phases in the sub-surface environment.
- Density and viscosity control mobility. Whilst density controls buoyancy behaviour at the water table and is directly related to the head pressure an NAPL can exert at a specific location.

The purpose of this manuscript is to examine, in detail, how these properties affect NAPL transport and fate, and a major goal of the manuscript is to identify and explore the molecular and physical chemical basis of these properties.

Understanding the sub-surface environment

Before we can examine the constraints that the physico-chemical properties of NAPLs exert upon their transport and fate, we need to explore the salient features of the sub-surface environment, the environmental medium within which they are normally released.

Soils are complex mixtures of:

- inorganic particles derived from the chemical, biological, and physical erosion of sub-surface rocks;
- biota including bacteria;
- organic matter derived from dead bacteria, plants, and animals;
- liquids most commonly water;
- gases including oxygen, carbon dioxide, and methane.

Soils are unconsolidated porous media. This means that soil particles are not irreversibly cemented together and the particles form a network of interconnected pores. Particle size is an important defining parameter. Sand particles range in size from 2.0 to 0.05 mm, silt particles are defined as particles with a size range of 0.05–0.002 mm, and clay particles are particles that are less than 0.002 mm in size. Soils have a variable composition with respect to these particle size classes.

If we explore far enough down a soil profile, we eventually reach a stratum composed entirely of rock, referred to as bedrock. Rocks may be igneous, metamorphic, or sedimentary. Igneous rocks are derived from cooling magma (a mixture of liquid silicates, crystals, and vapour bubbles). Sedimentary rocks are formed by the sedimentation of eroded rock particles or the skeletal remains of marine creatures in water bodies that are subsequently buried and cemented together. Metamorphic rocks are formed by the action of heat and pressure upon existing rocks.

Rocks and soils are porous, which signifies that both NAPLs and water contaminated with NAPL components can potentially flow through them. In unsaturated porous media, volatile NAPL components can also migrate, via the vapour phase, through interconnected pore spaces.

For rocks, we can identify two types of porosity: primary porosity—the porosity that originally existed in the rock type and secondary porosity that is created by fracturing and faulting in rock formations. Primary porosity is important in sedimentary rocks, where the pore spaces between grains have been preserved from the initial sedimentation

event. Primary porosity in igneous and metamorphic rocks, on the other hand, is either very low or non-existent. All rock formations may show evidence of the development of secondary porosity as a result of geological stresses related, very often, to tectonic events. Extensive interconnected fracture networks can be extremely important in the transport of NAPLs or NAPL contaminated groundwater over large distances from the point of release in rock formations.

Infiltrating water derived from rain or snowfall migrates through the interconnected pores of soils and rocks. Downward migration is halted by the appearance of either an impermeable rock or clay barrier. It should be stressed that both the rock and clay maybe porous. That is, they may contain interconnected pore spaces or fractures, but the ability of fluids to migrate through the medium (described as permeability) is seriously hampered by the tightness of the pore spaces or fractures. There is, thus, a crucial distinction between porosity and permeability—although the absence of porosity signifies absolute impermeability.

At the boundary between a permeable zone and a low permeability or impermeable zone, water will accumulate. This permanent accumulation of water gives rise to what is referred to as the saturated zone. In this zone, both primary and secondary porosity are filled with water. The water in this zone is often referred to as groundwater to distinguish it from surface water encountered in lakes and oceans. Groundwater is an important resource and is used throughout the world as a source of potable water. Groundwater may be encountered at variable depths in the sub-surface. In the UK, deep fractured chalk formations are particularly important sources of groundwater that are used for domestic water needs.

Capillary forces: surface tension, interfacial tension, and contact angle

It is widely appreciated that a water surface behaves much like a stretched elastic membrane. This phenomenon described as surface tension accounts for the ability of insects such as pond-skaters that are denser than water to walk across a pond surface. At the molecular level, the formation of a surface is energetically unfavourable. Figure 1 depicts the schematic arrangement of molecules comprising a liquid. In the bulk, each molecule occupies a lattice position, wherein approximately six near neighbours surround it. At the surface, the number of near neighbours is reduced to five. The removal of the sixth neighbour is the free energy penalty paid when a surface is formed.

Figure 1 shows very much a simplification of what a liquid surface must be like. The surface region is the region, where we go from a condensed phase to the vapour phase. Properties such as density must undergo a smooth transition from values characteristic of a liquid to values
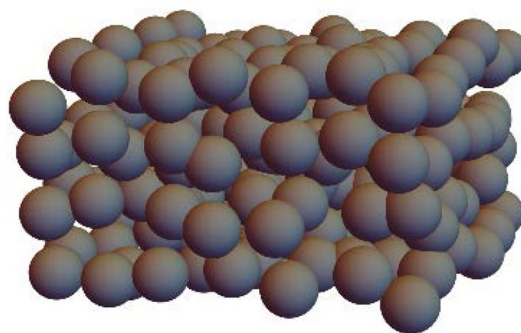

Fig. 1 Model depiction of molecules in a liquid

characteristic of a vapour over distances of less than a few nanometres. Such a transition implies that molecules are moving away from each other, at the surface, which requires energy to overcome the attractive forces between the molecules. The work necessary (δw) to increase the areal size of a surface (δA) is given by

$$\delta w = \sigma \delta A, \tag{1}$$

where σ is the surface free energy (units mJ m^{-2}).

It seems likely that there ought to be some relationship between the energy penalty associated with the formation of a surface and the existence of the elastic restoring force that characterises surface tension. In fact, the free energy penalty of surface formation per unit area is numerically equal to the surface tension (units mN m^{-1}) for liquids. Indeed, their units are equivalent (1 mJ m$^{-2} \equiv$ 1 mN m^{-1}).

However, the question remains: how does surface tension arise from the loss of near neighbour interactions in the surface molecular layer? Berry [3] and Hunter [4] have shown that to answer the question, we need to consider the variation in pressure in the liquid and vapour phases and the surface region. To understand their argument, we need a better model of the disposition of molecules in the liquid and vapour phases. This is shown in Fig. 2.

The figure shows that in the condensed liquid phase, the molecules are loosely packed. Intermolecular interactions are responsible for the packing; thermal energy is responsible for the looseness of that packing. The surface shown as the blue rectangle represents in a very arbitrary fashion the boundary between the liquid and vapour. In reality, the surface is ill-defined, and in all probability, there exists an interfacial region shown as the volume element between the blue and red rectangles. In the vapour phase, intermolecular interactions are negligible, and thus, its density is low. The density of molecules in the interfacial region is larger than the density of molecules in the vapour phase, because there is still some intermolecular interaction across the surface.

In a fluid, at equilibrium, pressure can be defined as the time averaged normal force per unit area of all molecules on one
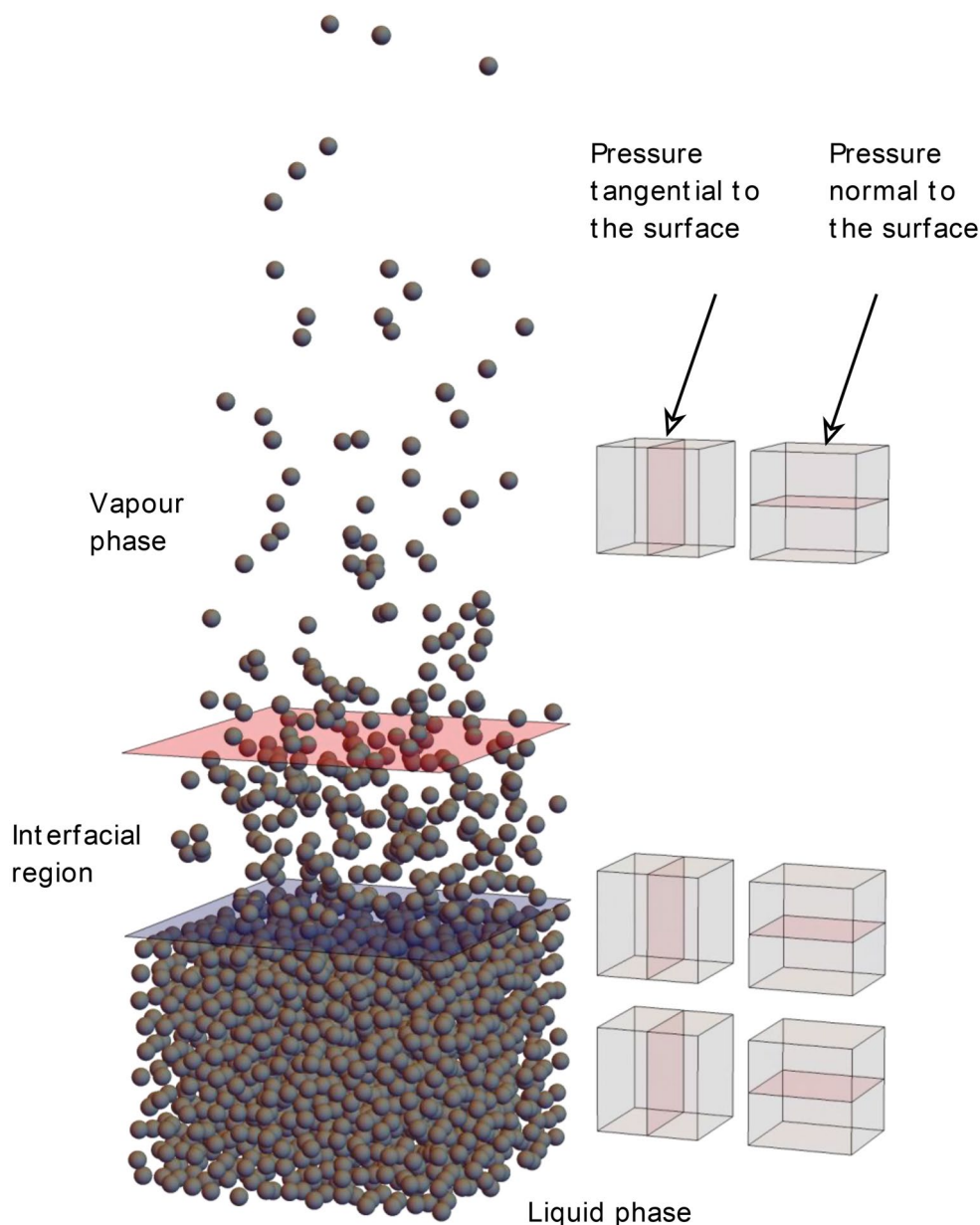
Fig. 2 Model showing the arrangement of molecules in the liquid, and vapour phases and the surface region. Also shown are the imaginary test cubes used to examine how pressure acting either normally or tangentially to the surface varied as we go from the liquid phase to the vapour phase. Note well: the pressure of interest acts perpendicularly to the red rectangles located inside the cubes

side of a small imaginary test surface on all those on the other side [3]. In Fig. 2, this test surface is shown as the red rectangles in the cubes. The pressure consists of two parts. The first is the kinetic contribution that comes from the thermal energy possessed by the molecules and is given by the equation:

$$p_k = \rho kT, \tag{2}$$

where ρ is the density of the fluid, k is Boltzmann's constant, and T is the absolute temperature. The kinetic contribution to pressure in the liquid phase is greater than that in the gas phase, because the density is greater (as shown in Fig. 2).

The second pressure component arises from the static forces of attraction and repulsion that exist between molecules either side of the test surface. The static component must be greater in the liquid phase than in the vapour phase because of the greater number density of molecules in the liquid phase, because the molecules are closer. The total pressure is given by

$$p = p_k + p_s, \tag{3}$$

where the subscripts k and s indicate the kinetic and static components, respectively. The static component is normally

negative because of the attractive forces between molecules. In the bulk phases, pressure is isotropic, because the distribution of molecules—averaged over time—is symmetrical. However, at the surface, molecular distribution is asymmetric—there are far more molecules on the liquid side than the vapour side. This distribution is time invariant. This leads to an asymmetry in pressure.
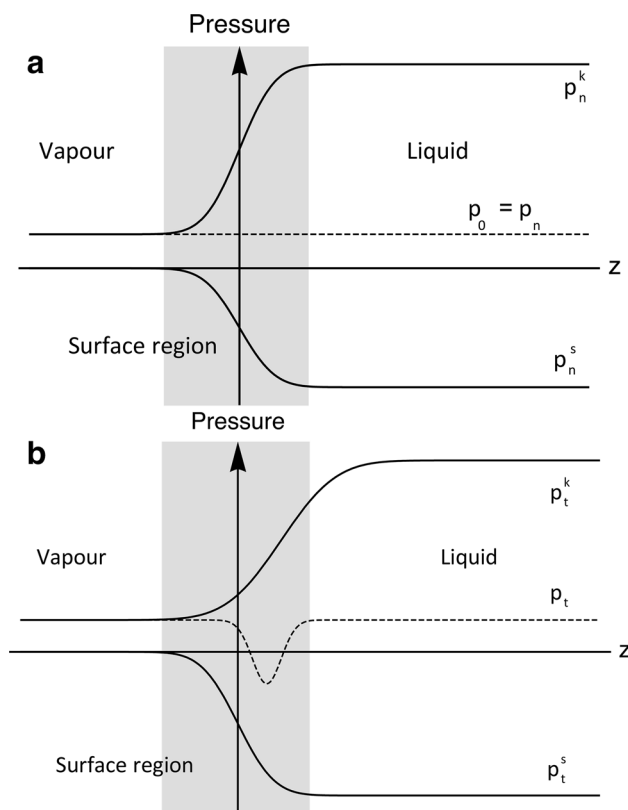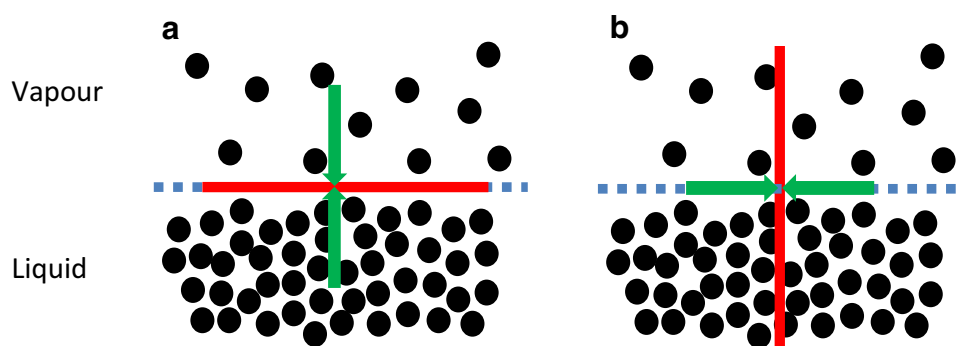
Consider Fig. 3, which shows the distribution of molecules at the liquid surface (shown as the blue dotted line). Of interest are the molecular interactions (shown as green arrows) acting across the imaginary test surfaces (shown in red). In Fig. 3a, the imaginary plane is drawn tangential to the surface and examines the static component of the pressure perpendicular to the liquid surface. The static forces of attraction are relatively weak, because there are far fewer molecules in the vapour phase. On the other hand, for the plane drawn perpendicular to the surface (Fig. 3b), the static component of pressure tangential to the surface is larger because of the greater number of molecules either side of the imaginary plane.

Let us now examine the consequences of this for the pressure in the infinitesimally small test cubes as we go from the vapour phase to the liquid phase via the interfacial region (shown in Fig. 2). To maintain mechanical equilibrium across the plane of the test cube, forces must be equal and opposite. The kinetic and static components of the normal pressure change smoothly from their high values in the liquid phase to their lower values in the vapour phase, as shown in Fig. 5a.

For the pressure acting perpendicularly to the surface, these changes must scale proportionately. In the vapour phase, the number density of molecules is small, so the kinetic and static components of the pressure are correspondingly low. In the liquid, both components are high, and in the interfacial region, both components change proportionately. The liquid surface is parallel to the earth's surface, so the pressure, which is the sum of the kinetic and static components (shown as the dashed line in Fig. 4a), is equal to the external atmospheric pressure p_0 all the way through the liquid, surface, and vapour phase to maintain mechanical equilibrium.

This, however, is not true for pressure acting tangentially to the surface (shown in Fig. 4b). At the surface, the

Fig. 4 Schematic depiction of the changes in kinetic and static pressure contributions to the normal (**a**) and tangential (**b**) pressure, on moving from the liquid phase to the vapour phase, via the surface region

pressure acting perpendicularly is greater than the pressure acting tangentially because of the numerically larger static contribution to the tangential pressure (as shown in Fig. 4b) for the reasons explained in Fig. 3b. The kinetic contribution to the pressure, on the other hand, must be the same for both the normal and tangential pressure, because the number density of molecules is exactly the same. Thus, the pressure acting tangentially is lower at the surface than the external pressure, as shown by the dashed line in Fig. 4b.

Fig. 3 Molecular interactions across an imaginary plane (shown in red) at a liquid surface shown in blue

Liquid	Surface tension (mN m^{-1})
Hexane	18.4
Tetrachloromethane	26.9
Benzene	29.0
1,2-dichloroethane	32.2
Water	72.8
Mercury	484.0
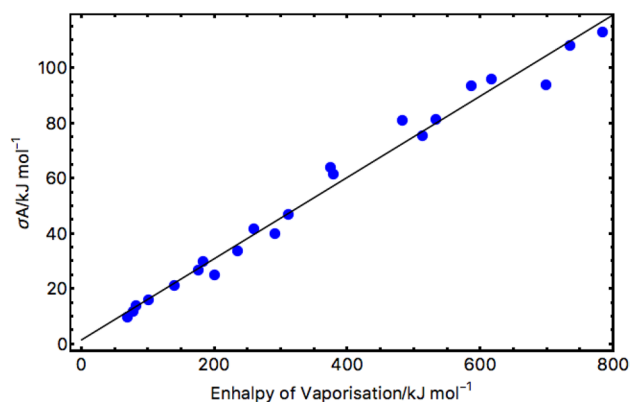
Fig. 5 Graph displaying the linear relationship between surface tension multiplied by the atomic surface area and the enthalpy of vaporisation for a series of molten metals. Data obtained from reference [5]

It is this pressure deficit that gives rise to surface tension. It must be emphasised that this is not an unbalanced force, but the necessary restoring force is applied externally [4]. This may come from the elastic deformation of the walls of the container within which the liquid is held or for an isolated droplet, it will come from the increased hydrostatic pressure within the droplet.

The strength of the intermolecular bonds between molecules in a liquid and the energy necessary to transfer molecules from the liquid phase to the vapour phase must provide a clue as to the size of the surface tension of the liquid. Molecules held together by London dispersion forces have comparatively low surface tensions. This is shown by the data presented in Table 1 for octane. Molecules which have some polarity either because of the presence of electronegative chlorine atoms in tetrachloroethane and 1,2-dichloroethane; or because of the delocalised electron cloud in benzene have slightly larger surface tensions. Water whose molecules are held together by both van der Waals and hydrogen bond forces has a much higher surface tension. Whilst mercury, which is held together by metallic bonds, possesses a very high surface tension.

One feature of the liquid surface model shown in Fig. 2 is that in the interfacial region, the molecules comprising the liquid phase are beginning to move apart. This requires energy. Indeed, the formation of the interfacial region is an intermediate point in the formation of the vapour phase. Thus, we might expect there to be a linear relationship between the work of forming the surface (surface tension multiplied by molar surface area of the liquid atoms) and the enthalpy of vaporisation.

Figure 5 displays data obtained for a range of metals in the molten state [5, 6] and gratifyingly demonstrates the existence of a linear relationship between the two variables. The enthalpy of vaporisation is the energy required to separate molecules from each other and is, therefore, directly related to the size of the intermolecular forces between the molecules. The linear relationship also corroborates the observation that the strength of the intermolecular interactions between the atoms is directly proportional to the size of the surface tension.

The gradient obtained is approximately 0.15 and suggests that the energy difference between vaporisation and forming a surface is 6.8. That is 6.8, as many bonds are broken on vaporisation as on surface formation. This suggests that the formation of a liquid surface requires the breaking of approximately one intermolecular bond, since vaporisation involves the separation of one central atom from its nearest neighbours which in the case of a primitive cubic, lattice is 6, and for a body-centred cubic, lattice is 8. If the average coordination number in the liquid state is less, then the number of bonds broken as part of surface formation is larger.

It should be noted that an interfacial tension also exists at the boundary between two immiscible liquids. Immiscibility implies that there exists an energy penalty associated with breaking intermolecular bonds between molecules of liquid A and forming intermolecular bonds with molecules of liquid B at the interface between both liquids which is not compensated for by the entropy of mixing. For example, at the interface, between water and hexane hydrogen bonds in water are broken to form weaker van der Waals interactions with hexane molecules. The static contributions to the normal pressure in this case are larger because of the larger number of molecules on both sides of the interface and because of the existence of the van der Waals interactions. However, the static component of the tangential pressure is greater, because the forces of attraction (the interactions between across the plane shown in Fig. 3b) are augmented by the hydrogen bonding in the water phase. Thus, once again, a pressure deficit exists at the interface which gives rise to an interfacial tension.

The Young Laplace equation and capillary pressure

In the previous section, it was noted that because of the pressure deficit in the static component of the tangential pressure, there is an increase in hydrostatic pressure inside a liquid drop. Indeed, a pressure jump always exists at any curved interface between two immiscible fluids with the pressure on the concave side of the interface being greater than the pressure on the convex side. The relationship between the pressure jump, curvature, and surface/interfacial tension can be derived in the following way.

Consider Fig. 6, which shows the expansion of a curved surface between two immiscible fluids such as a liquid drop in contact with air. The pressure inside the drop responsible for expansion is p_i. The drop expands against an external air pressure p_a. The increase in area when the surface is displaced is given by

$$(x + dx)(y + dy) - xy = xdy + ydx. \tag{4}$$
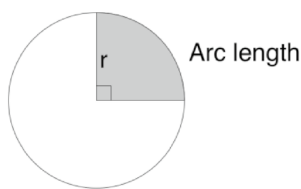
In this diagram it readily deduced that the arc length is one quarter of the circumference. $\frac{2\pi r}{4} = \frac{\pi}{2} r$. The angle at the origin between the two radii that extend to either end of the arc is 90° or $\frac{\pi}{2}$ radians. The arc length is therefore given by the radius multiplied by the angle in radians at the origin between the two radii that extend to either end of the arc.

The term $dxdy \rightarrow 0$ and so is ignored. The work done on expansion (see Eq. 1) is thus given by

$$dw = (xdy + ydx)\sigma, \tag{5}$$

where σ is the surface tension between the liquid and air.
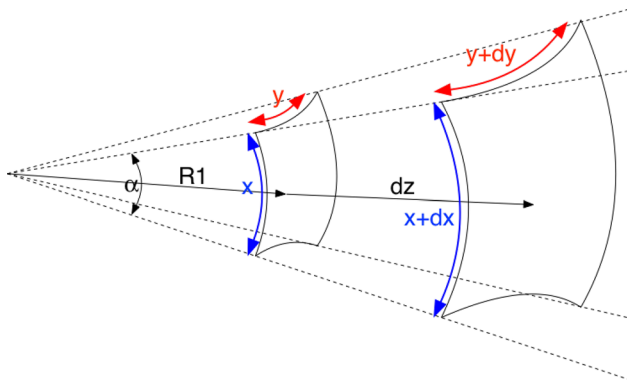
Fig. 6 Geometric figure used for the derivation of the Young Laplace equation. The figure is derived from reference [7]

If ordinary pressure volume work is responsible for expansion, then we can write that the work done is given by

$$dw = \Delta p dV. \tag{6}$$

The change in volume is given by

$$\begin{aligned} dV &= (x + dx)(y + dy)dz \\ &= xydz + xdydz + ydxdz + dxdydz \\ &= xydz. \end{aligned} \tag{7}$$

We can ignore those terms in Eq. (7) that contain the product of two or more derivatives, since they are vanishingly small. The resultant expression for the change in volume can be substituted into Eq. (6) to provide an expression for the work of expansion of the surface which is then equated with Eq. (5):

$$(xdy + ydx)\sigma = \Delta p(xydz). \tag{8}$$

What is the relationship between the arc length, x, the radius of curvature, R1 and the angle, α?

The required relationship is straightforward: $x = R_1\alpha$. We also note that $(x + dx) = (R_1 + dz)\alpha$, which means that by rearranging each equation to provide an expression for α and then equating both expressions, we obtain

$$\frac{x + dx}{R_1 + dz} = \frac{x}{R_1}. \tag{9}$$

Which can be simplified to give

$$\frac{dx}{xdz} = \frac{1}{R_1}. \tag{10}$$

Similarly, if the radius of curvature for the arc length y is R_2, then we can write

$$\frac{dy}{ydz} = \frac{1}{R_2}. \tag{11}$$

If we rearrange Eq. (5) and substitute Eqs. (7) and (8), we get

$$\Delta p = \frac{(x\mathrm{d}y + y\mathrm{d}x)\sigma}{(xy\mathrm{d}z)}$$
$$= \left(\frac{\mathrm{d}y}{y\mathrm{d}z} + \frac{\mathrm{d}x}{x\mathrm{d}z}\right)\sigma \qquad (12)$$
$$= \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\sigma.$$

This is the general form of the Young Laplace equation and shows that the pressure difference between the interior and exterior of a curved fluid interface is directly proportional to the surface tension and the principal radii of curvature of the surface. This pressure difference is important, because it provides an explanation for the phenomenon of capillary rise.

Figure 7 shows in a schematic way the principle of capillary rise. It should be emphasised from the start that the liquid meniscus in the capillary is curved. In addition, importantly, the curvature is concave on the air side of the interface. Let us now consider the following pressure relationships.

The pressure at points A and B is atmospheric pressure. The height difference between A and B is of the order of a few cm; thus, there is an insignificant difference in atmospheric pressure between both points. The pressure P_1, which is measured just below the liquid surface, will be at atmospheric pressure. P_2, which is measured at the same elevation as P_1 in the liquid, is also at atmospheric pressure. P_3 must, therefore, be less than atmospheric pressure. The pressure difference across the meniscus inside the capillary is given, as we have seen, by the Young Laplace equation:

$$\Delta p = p_\mathrm{a} - p_\mathrm{w} = \frac{2\sigma}{r}. \qquad (13)$$
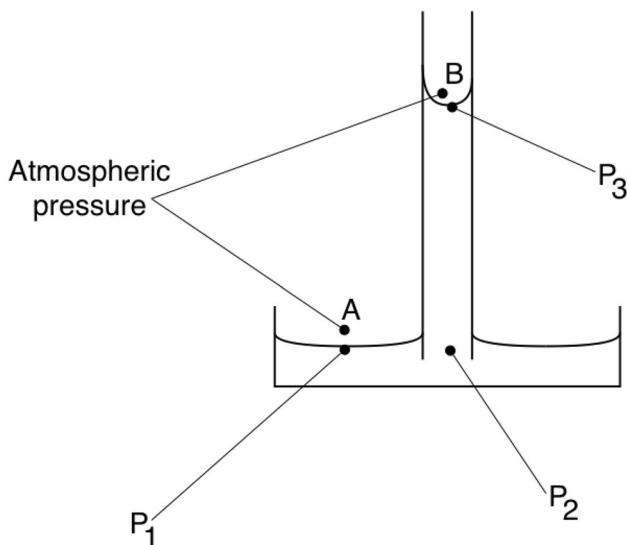
Fig. 7 Capillary rise diagram showing pressure at various points in the system

The subscripts a and w denote air and water, respectively. It is assumed that the meniscus is described by a perfect hemisphere that just fits inside the capillary, with the sides of the capillary tangential to this hemisphere, so that the principal radii of curvature of the meniscus, R_1 and R_2, are equal to each other and both are equal to the radius of the capillary, r.

We can thus state that the reason why water rises in a capillary is due to this pressure difference. When the capillary is first placed in the water reservoir, p_3 is located at the same elevation as p_1. Since $p_1 > p_3$, water moves along the pressure gradient, thereby raising the meniscus until the head of water plus the pressure p_3 are equal to p_1.

Very often, the angle made by the liquid meniscus to the capillary wall is not zero. The diagram shown in Fig. 8a shows a tangent drawn to the meniscus which intersects the three-phase contact line (i.e., the point, where liquid, air, and glass all meet. The two-dimensional diagram shows this as a point. However, in three dimensions, this is a line). The angle θ is called the contact angle. In this case, where the contact angle is not zero, the radius of the capillary does not describe the radius of curvature of the meniscus, and as a consequence, the pressure difference equation (Eq. 13) needs to be modified.

What is the relationship between the radius of curvature of the meniscus, the capillary radius and contact angle? This is easily answered using the geometric diagram displayed in Fig. 8b. In the figure, R is the radius of curvature of the meniscus, r is the capillary radius, and θ is the contact angle. The dashed line is the circle that describes the radius of curvature of the meniscus. The tangent that defines the contact angle is shown. Simple geometric principles show that the angle β is given by

$$180° = \theta + 90° + \beta$$
$$\beta = 90° - \theta. \qquad (14)$$

Since β is one angle of a right angle triangle, the adjacent angle along the hypotenuse must be θ. Thus, we can deduce that
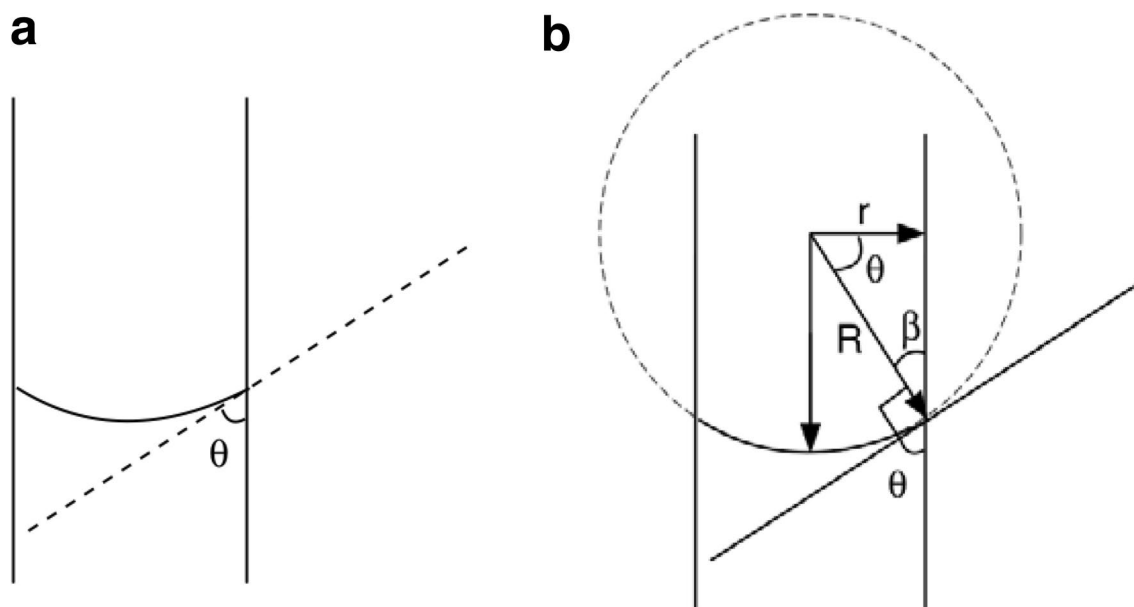
$$\frac{r}{R} = \mathrm{Cos}\,(\theta)$$
$$\frac{1}{R} = \frac{\mathrm{Cos}\,(\theta)}{r}, \qquad (15)$$

and the modified form of Eq. (1) which incorporates the effect of the contact angle thus becomes

$$\Delta p = \frac{2\sigma\,\mathrm{Cos}(\theta)}{r}. \qquad (16)$$

It is noteworthy that since the contact angle appears as a cosine function, the pressure difference is affected as θ changes value. If $\theta = 0°$, then $\mathrm{Cos}(\theta) = 1$ and the pressure

a

b

Fig. 8 **a** Cartoon showing a non-zero contact angle in a capillary and **b** relationship between the radius of curvature of the meniscus, the contact angle θ and the radius of the capillary

difference is a maximum for a particular value of surface tension and capillary radius. On the other hand, for a flat surface $\theta = 90°$, then $Cos(\theta) = 0$, there is no pressure difference, and thus, no capillary rises. Thus, it is important to stress that a pressure difference only occurs across a curved meniscus between the two immiscible fluids (in this case water and air), with the pressure being greater on the concave side of the meniscus.

The contact angle is very often referred to as the wetting angle. The cartoon shown in Fig. 9 readily illustrates the relationship between wetting and contact angle. In the case of the blue liquid, the contact angle made by the drop is less than 90°, thereby indicating that liquid does not spread across the yellow surface. On the other hand, a drop of red liquid clearly spreads which is shown by a contact angle greater than 90°.

Capillarity, adhesion, and fluid transport and disposition in porous media

When water enters a volume element of soil or porous rock, such as during a rainfall event, it readily displaces air. It is observed that, once the event is over, water will drain downwards from the large pores located in the system, as a result of gravitational forces, to the water table. Not all the water will drain from the system of interest. Porous soils and rocks have pores of capillary dimensions, and thus, we find water is retained:
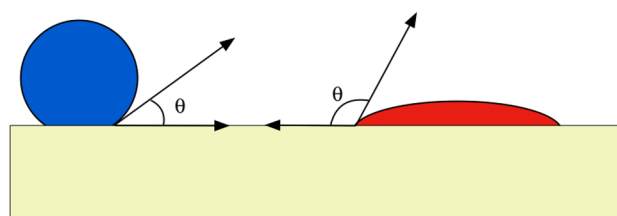
Fig. 9 Cartoon showing the contact angle for a non-wetting liquid (blue) and wetting liquid (red)

- as thin films covering soil or rock grains;
- as pendular water at the narrow contact regions between two or more grains—which are called pore throats;
- in small pores.

Examples of these are shown in cartoon form in Fig. 10. Water is held as thin films on solid soil surfaces, because water is, normally, the wetting fluid and thus spreads over the grain surfaces in competition with the air. Water is held at the contact points between grains and in small pores because of capillary forces. The curvature of the menisci in Fig. 11 indicates that the pressure inside the water phase is less than the pressure on the airside. Water is thus held in small pores by a kind of capillary suction, which is normally termed matric suction. Thus, the unsaturated zone shows variable water saturation that is related to grain size and grain size distribution. Small soil grains produce small pores and pore throats, which are much better at retaining water through capillary action.
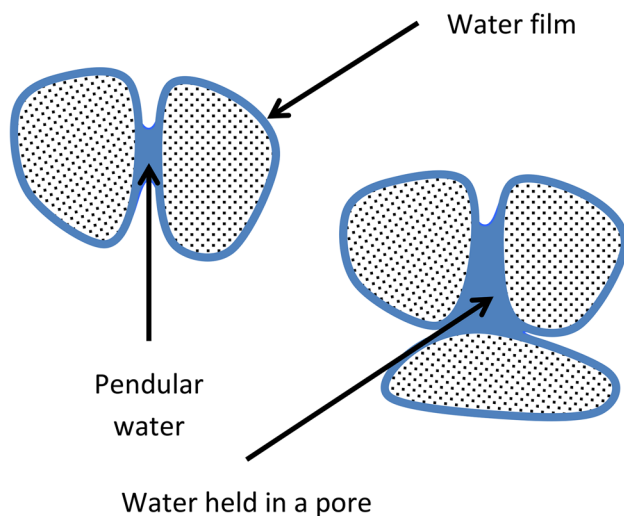
Fig. 10 Water in the unsaturated zone

Water may also accumulate in pores throats and small pores through capillary condensation. Capillary condensation arises from the fact that the vapour pressure at a concave liquid surface is lower than the vapour pressure at a flat liquid surface. Consequently, liquid condenses in a capillary at pressures lower than the saturated vapour pressure. The pressure reduction is given by the Kelvin equation (see reference [7] for its derivation).

Typically, an NAPL entering a soil system as a result of a spill, leakage from a storage tank or deliberate disposal, will readily displace air, in the unsaturated zone. Water held in small pore spaces and at pore throats by capillary forces is more difficult to displace. The pressure necessary to displace water is termed the entry pressure is described by a form of Eq. (16):

$$P_c = P_N - P_W = \frac{2\sigma \cos(\theta)}{r}, \tag{17}$$

where P_c is designated as the capillary pressure and is equal to the pressure difference between the NAPL (P_N) and water (P_W) phases. Thus, entry pressure is determined by the following inequality:

$$P_N > P_E + \frac{2\sigma \cos(\theta)}{r}. \tag{18}$$

The magnitude of the pressure necessary to displace water from a pore/pore throat is proportional to the magnitudes of the opposing water pressure and interfacial tension as well as the contact angle and inversely proportional to pore/pore throat size.

Thus, a spilled NAPL body, in both the saturated and unsaturated zones, will tend to migrate vertically downwards through coarse-grained material. However, when the NAPL body encounters a zone of capillary resistance such as provided by water held in a clay or silt layer—which is composed of smaller particles and as a consequence provides a greater entry pressure than the surrounding coarse-grained material—it will tend to migrate laterally along the pathway of least capillary resistance. Indeed, the defining characteristic of NAPL transport in the sub-surface is that NAPL spreads laterally, as it migrates downwards.

This behaviour can be simulated by the use of the following crude numerical model created using Mathematica. The output of the model is shown in Fig. 11. The model is composed of a region of relatively large pores (mean size 0.0015 m, standard deviation 0.007 m) and three regions of smaller pores (mean size 0.007 m, standard deviation 0.0007 m). A matrix of pore sizes was generated stochastically, assuming that the distributions of pore sizes were described by a Gaussian distribution. From this, a matrix of pore throats (the linkage between two adjacent pores) was generated. The size was set as half the size of the smaller of the two adjacent pores. The disposition of the fine-grained and coarse-grained regions is shown in Fig. 11. The system is initially water saturated. An NAPL reservoir is located at the top of the system and water at the bottom. The pressure of the NAPL and water reservoirs is controlled, as would be the case in a physical model. The capillary pressure is set and compared with the entry pressure of each pore throat in the matrix. If the capillary pressure is larger than the entry pressure, NAPL enters the pore. This process is repeated until the system has come to equilibrium.

It should be stressed that the model does not really correspond to any real-world system, since it does not include flow. NAPL flow and the entry pressure is determined by the contiguous pressure head of NAPL and the opposing water pressure. The model does not take into account pore geometry and the impact this will have on the curvature of the NAPL/water interface and the corresponding impact upon capillary pressure. However, the model does try to examine some of the salient features of experimental laboratory systems, where a porous medium is held in a container attached at the top and bottom to two liquid reservoirs—one containing water the other NAPL. The pressure exerted by each liquid is carefully controlled so as to permit control of the capillary pressure.

The outputs from the model demonstrate that as the capillary pressure is increased, NAPL displaces water from the coarse-grained medium. However, it is unable to penetrate the lower permeability layers comprising finer-grained material. It is interesting to note that there are regions—even in the coarse-grained medium—where NAPL does not penetrate, because the capillary pressure is insufficient for entry. If the capillary pressure is sufficiently, high NAPL will enter the finer-grained layers.
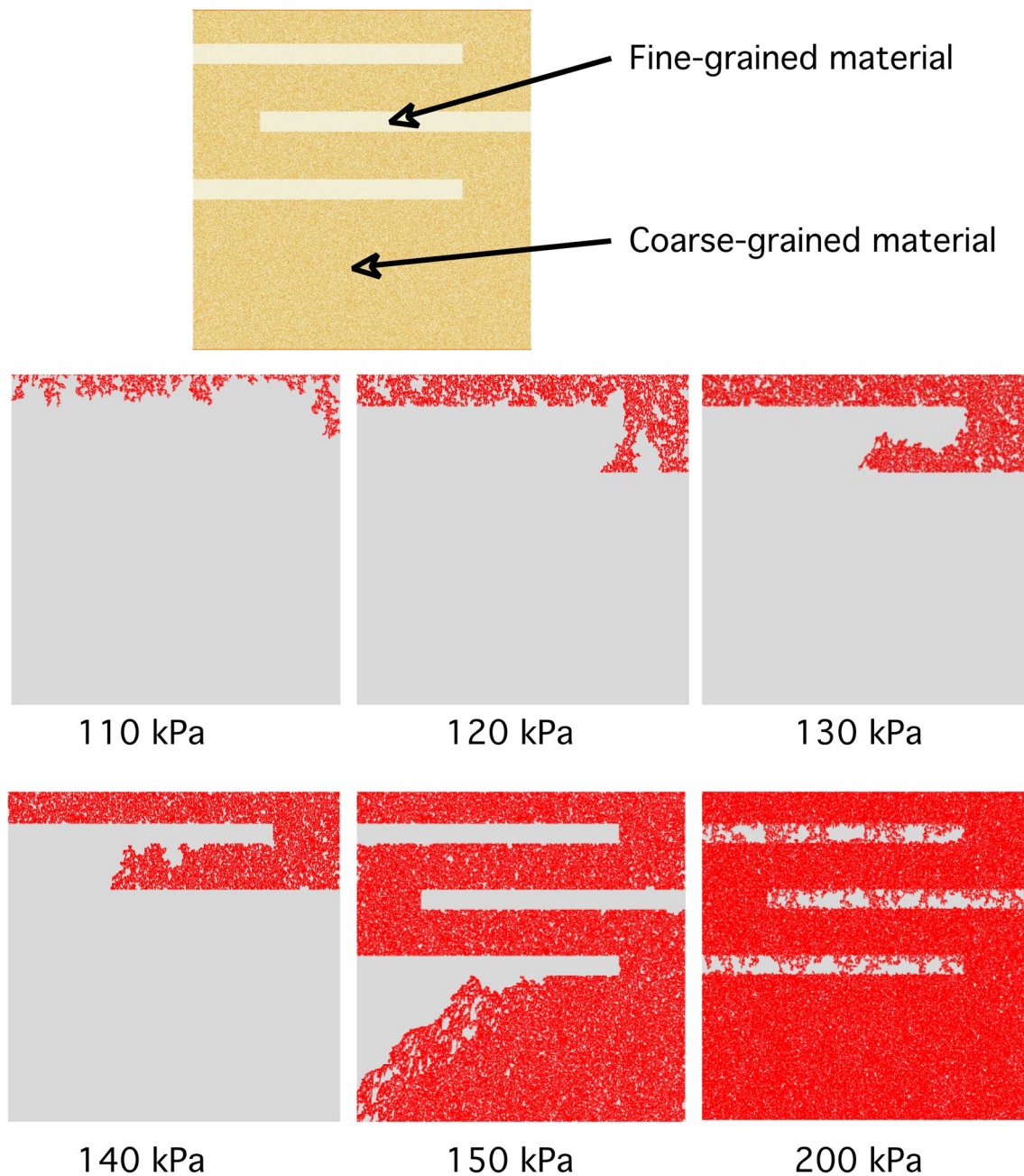
Fig. 11 Model showing how NAPL (in red) moves laterally over low permeability layers rather than penetrate them. The numbers under each figure are the values of the capillary pressure. It can be seen that if the capillary pressure is sufficiently high then NAPL will enter the capillary barriers

In the field, this would only happen if the head of NAPL was great enough.

We can calculate the NAPL pressure head in the following way:

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{\pi r^2 h \rho g}{\pi r^2}. \tag{19}$$

If we consider the NAPL to occupy a series of connected pores and pore throats and that at the contact region between NAPL and water, the NAPL body forms a circular interface of area πr^2, where r is the radius of the contact region. The volume of the cylinder of NAPL is then $\pi r^2 h$, where h is the vertical height of the NAPL body. To convert that into a mass, we multiply by the density of the NAPL (ρ), and to convert it into a force, we multiply by the gravitational
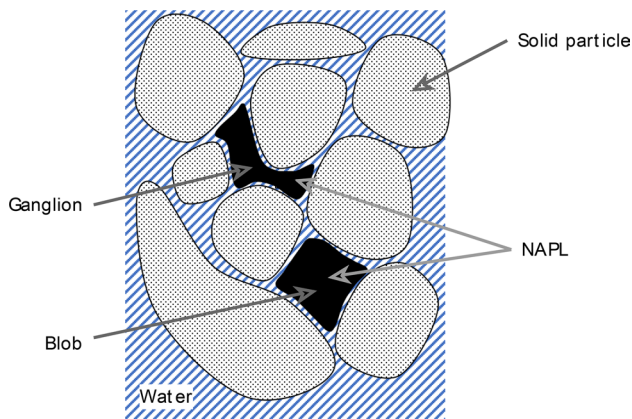
Fig. 12 Disposition of water, solid particles, and NAPL in the saturated zone. NAPL occupies large pores—because the entry pressure is relatively low—whilst water is located in the smaller pores, because the NAPL entry pressure is much larger

Fig. 13 Cartoon showing how adjacent layers in the liquid move at different velocities after the application of a sheer stress. The plates are assumed to be essentially infinitely long

acceleration constant (g). The area of the cylinder is πr^2, so the pressure head (hydrostatic pressure) is given by

$$p = \rho g h. \tag{20}$$

At the water table, density determines whether an NAPL will enter the saturated zone. DNAPLs can penetrate the water table, because their density is greater than that of water. LNAPLs, on the other hand, will depress the water table, but will not sink below it. LNAPLs will thus tend to spread across the water table.
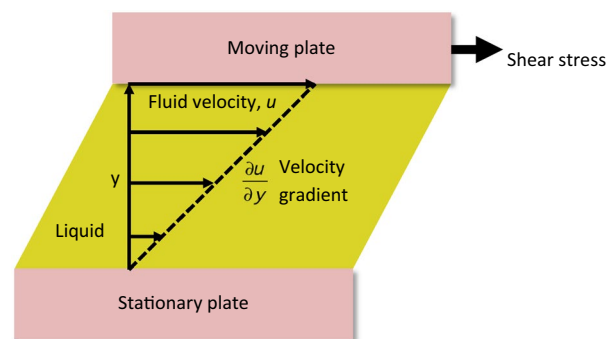
Pore scale hydrodynamic instabilities result in NAPL droplets becoming detached from the trailing edge of a migrating NAPL body as blobs or ganglia (Fig. 12). This occurs in both the saturated and unsaturated zones. Blobs are droplets trapped in single pore spaces.

Ganglia comprise several contiguous pores that are occupied by NAPL. Bobs and ganglia are immobile, trapped by in situ by capillary forces.

In some cases, potentially, mobile pools may form and accumulate. Pools consist of NAPL encountered as a continuous liquid in interconnected pore space and which are mobile given a sufficient driving pressure. Pooling may occur at:

- a capillary barrier, i.e., the boundary between coarse-grained and fine-grained layers;
- the boundary between an unconsolidated soil and a fractured rock layer;
- LNAPLs will also accumulate to form potentially mobile pools at the water table.

One important question regarding NAPL fate in subsurface soils and rocks is the question of how long does an NAPL body remains mobile. This is determined by the mass of NAPL released. A small mass is likely to be immobilised quickly, because capillary trapping of residual droplets from the trailing edge will rapidly deplete the mobile mass and thus reduce the head pressure exerted by the NAPL, so that it reaches a location, where NAPL entry pressure is greater than the NAPL head pressure.

However, viscosity also plays an important role in NAPL distribution. NAPLs possessing low viscosities travel relatively quickly and are stabilised (stop migrating) within timescales of weeks to months. More viscous NAPLs, on the other hand, may continue travelling over timescales of months to years.

Viscosity is determined, inter alia, by the magnitude of the intermolecular forces between the molecules comprising an NAPL.

Consider a liquid sandwiched between two parallel plates as shown in Fig. 13. If one plate is stationary and the other mobile then movement of the mobile plate results in the application of a shear stress to the trapped liquid. The liquid flows as a response to the stress. The layer adjacent to the moving plate moves at the velocity of the plate. The layer adjacent to the stationary plate does not move. This leads to the creation of a velocity gradient in the bulk liquid, wherein consecutive layers of liquid have increasing velocities, as we go further from the stationary plate. The practical upshot of this process is that adjacent layers move past each other. Their movement is opposed by frictional forces that arise from intermolecular forces. It is these frictional forces that are related to a liquid's viscosity. Water, for a small molecule, has a relatively high viscosity, 1.01×10^{-3} Pa s because of hydrogen bonding. Glycerol with its three OH groups has multiple opportunities for hydrogen-bonding interactions with other glycerol molecules and as a consequence has a viscosity 1.49 Pa s—three orders of magnitude greater. Propane molecules are also three carbon atoms long. They, however, interact with each other through weak London dispersion forces, and as a result, the viscosity of propane is

very low, 1.1×10^{-4} Pa s—some four orders of magnitude lower. All viscosities quoted were measured at 20 °C.

Viscosity is also determined by the size and shape of the molecules comprising the liquid. Compact molecules have fewer interactions than extended molecules and thus in general have lower viscosities. Flexible long-chain molecules can become entangled and thus have trouble moving past each other when the liquid flows. For example, coal tar, which is derived from the pyrolysis of coal as part of the process of making coke and coal gas, is a complex mixture of aliphatic and aromatic hydrocarbons, whose viscosity is augmented by the presence of high-molecular mass compounds called asphaltenes.

Mass transfer of NAPL components to the vapour and water phases

Trapped residual droplets and pools provide a source of both water and vapour pollution. They do this via mass transfer from the NAPL body to either the vapour or aqueous phases. Molecules are transferred from the liquid body to the vapour phase via vaporisation and to the aqueous phase via solubilisation. The transport mechanism, in both cases, relies upon random motion, arising from thermal energy, of molecules that is constrained by intermolecular interactions.

This random thermal motion is the molecular basis of diffusion. Diffusion is the process, wherein at a phenomenological level, molecules move from a region of high concentration to an adjacent region of lower concentration. However, the actual mechanism is solely reliant upon random molecular motion. This is readily demonstrated by the use of a simple lattice model within which a central region of the lattice is occupied entirely by a particular molecule (shown as red in Fig. 14). The red molecules are then allowed to move to a stochastically chosen adjacent lattice site. The result of this random process is the gradual spread of the red molecules throughout the available volume. In thermodynamic terms, we see this as a manifestation of increasing entropy.

Diffusive flux, N—the amount of material transported per unit time (units M T^{-1}) is described by Fick's first law of diffusion:

$$N = -DA\frac{dc}{dx}, \tag{21}$$

where D is the diffusion coefficient (L^2 T^{-1}), A is the cross-sectional area through which diffusion occurs (L^2), and the differential term represents the concentration gradient (M L^{-1}). The negative sign arises, because the concentration gradient is negative—material flows from high concentration to low concentration. Indeed, all potential gradients along which matter or energy flows spontaneously must be negative.

The mixing of the molecules comprising the NAPL with either the vapour phase or aqueous phase is entropy driven. What attenuates the drive towards a complete mixing is the control exerted by intermolecular forces. For vaporisation, molecules are able to escape the condensed liquid phase only if their thermal kinetic energy is greater than the energy necessary to break the intermolecular bonds holding the molecule in the liquid phase. Once escaped, they freely mix with molecules already present in the vapour phase, because there are no opposing intermolecular barriers to mixing.

The solubilisation of NAPL components, on the other hand, has an additional constraint. Not only is it regulated by the breaking of bonds in the aqueous and the NAPL phases, but it is also critically dependent upon the formation of new bonds between the aqueous phase and the NAPL molecular component—as shown in Fig. 15.

As noted previously, we recognise that all chemical processes are spontaneous if the free energy change (which may also be described as a chemical potential gradient) for the process is negative. In other words, if the free energy of the final state is lower than the free energy of the initial state, then the process is spontaneous.

The Helmholtz-free energy (F) is made up of two components:

$$\Delta F = \Delta U - T\Delta S, \tag{22}$$

where U is the internal energy of the system, T is temperature, and S is entropy. It is worth recalling that internal energy change is the heat change in the system at a constant volume. If we examine the heat change at a constant pressure, wherein the system can also perform so-called PV work, then Eq. (21) would be modified by the replacement of

Fig. 14 Lattice model used to demonstrate how diffusion is mechanistically regulated by random thermal motion

Time ⟶
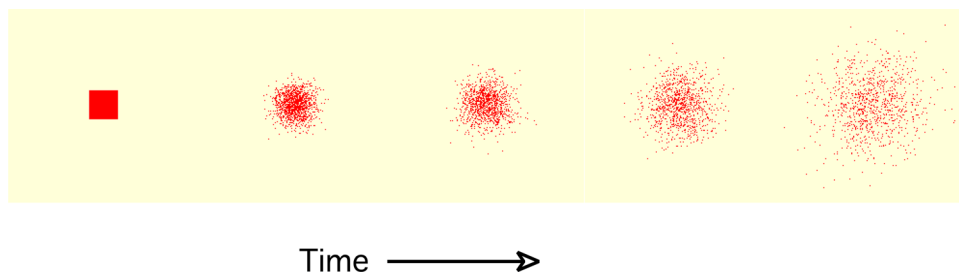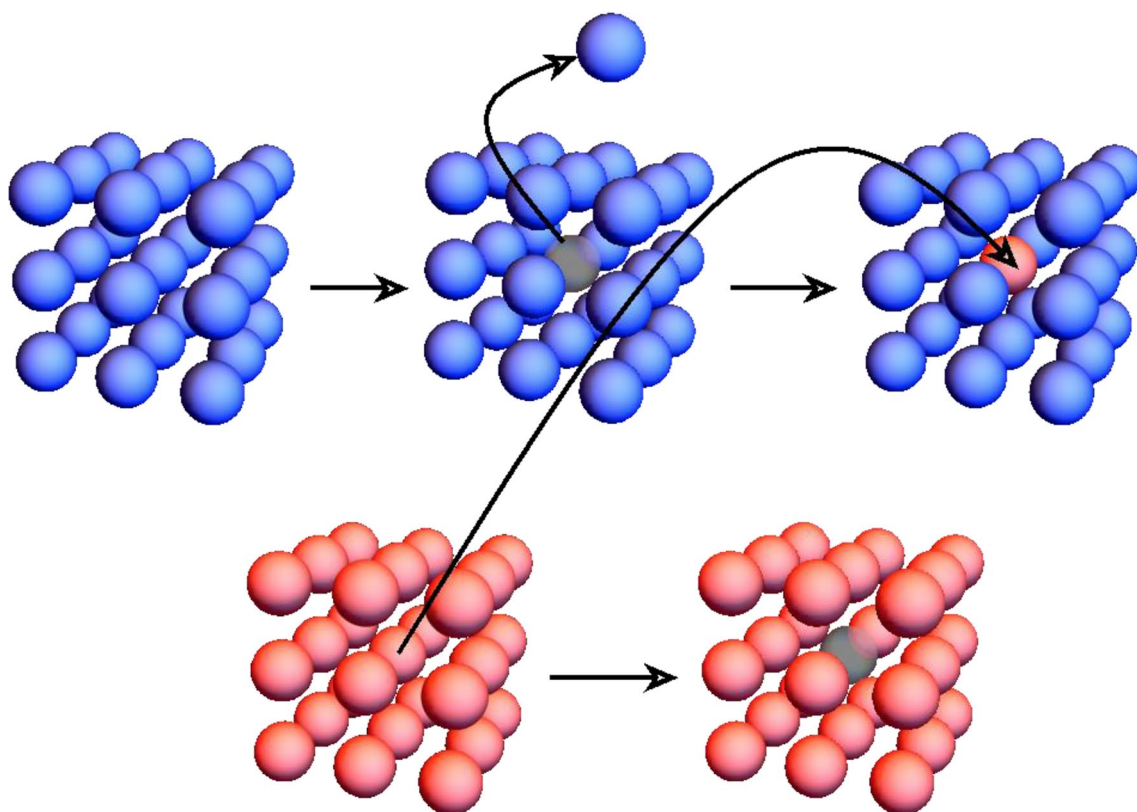
Fig. 15 Cartoon showing that solubilisation of NAPL molecules (red) in the aqueous phase (blue) requires the formation of a cavity through the removal of a molecule to the surrounding bulk phase. This requires the breaking of water–water bonds. An NAPL molecule is then transferred from the NAPL phase to the cavity in the aqueous phase which again requires the breaking of intermolecular bonds. Once in the cavity, new intermolecular bonds are formed

the internal energy term by enthalpy (*H*) and the Helmholtz-free energy is replaced by the Gibbs-free energy (*G*).

The dispersal of NAPL molecules in the vapour or aqueous phases results in an increase in entropy. The internal energy term represents the breaking and formation of intermolecular bonds. For an ideal solution, where the molecules of liquid A are equally at home in liquid B and vice versa, the energy required to break bonds and the energy released on creating new bonds are equal resulting in no change in the internal energy. In this particular case, solution formation is purely driven by the increase in entropy. Usually, though solution formation results in a non-zero internal energy change. A positive internal change represents the case, where the energy needed to break A–A and B–B intermolecular bonds is greater than the energy released by the formation of A–B intermolecular bonds. In this case, the liquids form two separate phases and have limited mutual solubility. They display what is described as a miscibility gap, wherein miscibility only occurs when the mole fraction of one of the components is exceedingly small. A negative internal energy change is representative of the case, where the formation of A–B intermolecular bonds results in a greater energy release than the energy required in the breaking of A–A and B–B intermolecular bonds. In this case, the liquids are completely miscible and solution formation is exothermic.

When examining the environmental fate of NAPLs at the molecular level, we usually make the simplifying, but normally, erroneous assumption that a multi-component NAPL is an ideal solution. This makes it much easier to predict the aqueous solubility and vapour pressure of components present in the NAPL.

Chemical parameters characterising the partitioning of molecular components from the NAPL to the vapour and aqueous phases

To properly understand the fate of chemicals in the environment, we need to be able to characterise their transfer from the source of their release to and between the dominant compartments that comprise the environment—namely air, water, soil, and biological. For NAPLs (the pollution source) in the

sub-surface environment, this means that we need to be able to quantify the transfer of NAPL components from the NAPL phase to either the soil, aqueous, or vapour phase.

Transfer occurs, because molecules present in the NAPL phase have a high chemical potential. Chemical potential (μ_i) is the partial molar free energy of component i in the NAPL solution and is defined as

$$\mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T,V,n_j \neq n_i}, \tag{23}$$

where n_i is the number of moles of component i.

Transfer to adjacent phases results in a reduction in the chemical potential. Concomitantly, the chemical potential of the compound in the adjacent phases increases. Thermodynamic equilibrium occurs when the chemical potential in each phase is equal. Thus, transfer in the environment occurs along pathways that reduce chemical potential.

Transfer of an NAPL component from the NAPL to the vapour phase is controlled by the vapour pressure of the component. For a component in an NAPL mixture, the vapour pressure exerted will be less than the vapour pressure above the pure liquid component.

Consider a multi-component NAPL. If we assume that it forms an ideal solution, then the chemical potential of component i in the NAPL is given by [8]

$$\mu_i(\text{soln}) = \mu_i°(\text{l}) + RT \ln(x_i), \tag{24}$$

The term $\mu_i°(\text{l})$ represents the standard chemical potential of the pure liquid and x_i is the mole fraction of component i in the NAPL solution mixture.

For the vapour phase, we can write

$$\mu_i(\text{g}) = \mu_i°(\text{g}) + RT \ln(p_i). \tag{25}$$

Here, p_i is the partial pressure of component i in the vapour phase and $\mu_i°(\text{g})$ is the standard chemical potential of the vapour. At equilibrium, $\mu_i(\text{soln}) = \mu_i(\text{g})$. Thus, by equating Eqs. (22) and (23) and rewriting the resultant expression, we obtain

$$p_i = x_i \exp \left(\frac{\mu_i°(\text{soln}) - \mu_i°(\text{g})}{RT} \right). \tag{26}$$

If we apply Eq. (26) to a pure liquid then $x_i = 1$ and $p_i = p_i^*$, the vapour pressure of the pure liquid. Equation (26) can then be rewritten as

$$p_i^* = \exp \left(\frac{\mu_i°(\text{soln}) - \mu_i°(\text{g})}{RT} \right)$$
$$p_i = x_i p_i^*. \tag{27}$$

Equation (27) is a statement of Raoult's law. Raoult's law is valid only for ideal solutions, though it does, in general,

describe solvent behaviour in sufficiently dilute solution. This would be expected, since as the solution becomes more and more dilute, the majority of solvent molecules increasingly find themselves in contact with other solvent molecules. On the other hand, as the solution becomes increasing dilute, the solute molecules find themselves increasing surrounding by solvent molecules. Under these circumstances, Raoult's law does not hold for the solute. However, it is generally noted, in experimental studies, that the vapour pressure of the solute does increase linearly with mole fraction of solute in dilute solutions. It is just that, unlike in Eq. (27), the constant of proportionality is not the vapour pressure of the pure solute. In practice, the following equation can be written

$$p_{\text{solute}} = K_\text{H} x_{\text{solute}}, \tag{28}$$

where K_H—the proportionality constant—is referred to as the Henry's law constant. In this formulation, K_H has the units of pressure, since mole fraction is dimensionless. The Henry's law constant is clearly an important parameter that characterises the partitioning of a solute between the vapour and aqueous phases. Henry's law constants can be measured, although it is often more convenient to calculate them using readily available physico-chemical data. Mackay [9] has suggested that a constant can be calculated using the saturated vapour pressure (p_{sat}) and saturated solubility (c_{sat})—which examines the partitioning of a solute between the aqueous and vapour phases—to give Eq. (29):

$$K_\text{H}' = \frac{p_{\text{sat}}}{c_{\text{sat}}}. \tag{29}$$

Clearly, in this formulation, this constant does not have the units of pressure hence the use of the prime. The saturated solubility can, however, easily be converted to a mole fraction if necessary. The Henry's law constant given in Eq. (29) is actually very convenient. We can use Eq. (29) in conjunction with Eq. (27) to estimate the aqueous phase solubility of an NAPL component if we assume that the multi-component NAPL forms an ideal solution. If we rearrange Eq. (29) and substitute the expression in Eq. (27), we obtain

$$s_i = x_i s_i^*, \tag{30}$$

where s_i is the aqueous phase solubility of component i, x_i is the mole fraction of i in the NAPL mixture, and s_i^* is the aqueous solubility of the pure liquid.

Thus, the thermodynamic driving force for transfer of components from the NAPL to the vapour and aqueous phases is the reduction in chemical potential. The mechanism, whereby the components are transferred from one phase to another, is slow molecular diffusion across the interface [9]. It is worth noting that turbulence in a phase will hasten the transfer of molecules to the interface, and

thus, the rate of transfer may be increased. It is unlikely, however, that the water flow in the sub-surface is sufficiently fast enough to induce turbulence. Vapour transport, however, may be turbulent under some circumstances related to gas velocity and the structure of the porous medium the gas is moving through.

## Transport in the water and vapour phases: advection, dispersion, and diffusion

The major environmental concern when dealing with NAPLs is their ability to transfer from an NAPL source zone to the vapour and aqueous phases. The NAPL source zone is the language we use to describe the presence of NAPL as a separate phase either in the form of residuals or pools. Normally, residual trapping by capillary forces in either pores or in fractures found in soil or rocks means that we have an immobile pollution source. NAPLs' pools are potentially mobile, but their immobility may be due to the absence of a significant hydraulic driving force, or due to accumulation in some sub-surface geological feature. The mass transfer of NAPL components to the mobile vapour and aqueous phases is an important pathway, whereby substances hazardous to health are transferred from the source zone to humans and other biotic and abiotic receptors.

The transport of NAPL components when dispersed in either the mobile aqueous phase or vapour phase is called advection. Bulk fluids move in the sub-surface environment in response to pressure gradients. If flow is laminar (Fig. 16), then bulk fluid transport is described by Darcy's law.

Darcy's law for water flow is written as

$$Q = -AK\frac{\Delta h}{\Delta l}, \tag{31}$$

where Q is the volumetric flow rate ($L^3 T^{-1}$), A is the cross-sectional area of porous medium through which water flows (L^2), and K is the hydraulic conductivity ($L T^{-1}$). The final term $\Delta h/\Delta l$ is the hydraulic gradient. Δh is the pressure
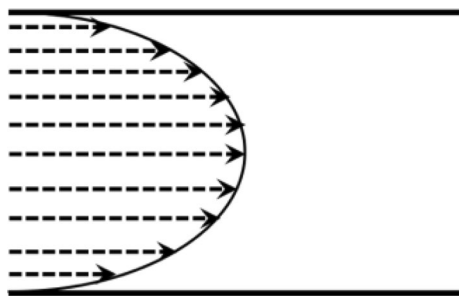
Fig. 16 Laminar flow. The horizontal arrows represent the flow lines that comprise laminar flow. The length of the lines corresponds to the fluid velocity

difference (measured as a head height—see Eq. 20) between two points separated by a distance of Δl. The negative sign appears, because the hydraulic gradient is negative—water flows from a high initial head to a lower head. The discerning reader will quickly appreciate that the Darcy's law equation is very similar to the Fick's law equation for diffusion. In both cases, matter moves down a potential gradient.

The hydraulic conductivity is related to the properties of the liquid and the porous medium the liquid flows through. Fetter [10] has provided the following equation:

$$K = K_i\frac{\rho g}{\eta}, \tag{32}$$

where ρ is the liquid density, g is the acceleration due to gravity, η is the liquid viscosity, and K_i is the intrinsic permeability. The intrinsic permeability is related to the porous medium through which the liquid flows and is related inter alia to grain size and shape. For the same porous medium, liquids with high densities and low viscosities (like chlorinated hydrocarbon solvents) are extremely mobile. On the other hand, liquids with lower densities and high viscosities (for example, crude petroleum and coal tars) move more slowly.

If we divide the volumetric flow rate (Q) by the cross-sectional area (A), we obtain an expression for the Darcy velocity $K\Delta h/\Delta l$. This is the rate at which water flows through a unit cross-sectional area. In practice, water does not flow through all the cross-sectional area—because much of it is occupied by solid particles. It can only flow through the interconnected pore spaces. Thus, the actual rate at which water flows through the system is given by

$$\text{Flow Rate} = \frac{K\frac{\Delta h}{\Delta l}}{\theta}, \tag{33}$$

where θ is the porosity of the medium and is the ratio of the volume of pore space to the total volume.

Water passing through an NAPL source zone dissolves NAPL components to form a relatively concentrated solution. Note carefully that the solution may be in practice extremely dilute. However, in the vicinity of the source zone, it will be more concentrated than it is down stream from the point of dissolution. The solute is clearly transported by the flowing water. However, the solute will also spread out due to diffusion—solute will spread from areas of higher concentration to lower concentration. The solute will also spread out because of dispersion. The mechanism of dispersion is shown in Fig. 17.

The amount of dispersion increases with the length of travel for the reasons, as shown in Fig. 18. In Fig. 18, we attempt to show the distance travelled, in specific time intervals, by solute molecules following particular pathways. In vignette "a", the time interval is short, and thus,
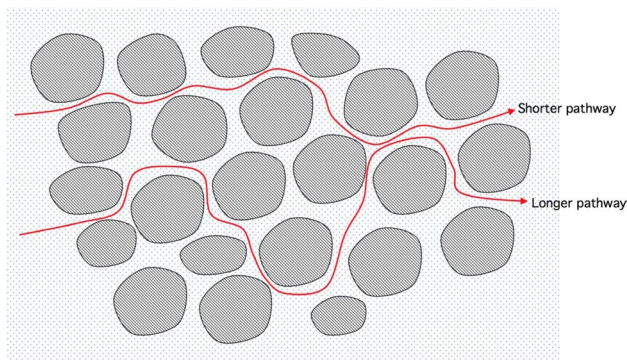
Fig. 17 Diagrammatic explanation for dispersion. Water flowing through a porous medium carries with it a solute. The solute molecules can travel along a variety of pathways (shown in red) some of which are more tortuous (and thus longer) than others

the length travelled is comparatively short and the difference between the two pathways is small. In vignettes "b" and "c", the time intervals are increasingly larger and the degree of dispersion becomes correspondingly greater.

We can use a modified version of the simple diffusion model that was developed earlier to show how a dissolved NAPL component behaves in flowing water. This is shown in Fig. 19.

The output shown in Fig. 19 was created using the diffusion model that was used to create the output, as shown in Fig. 14. In addition, flow was simulated by adding a randomly generated integer between 0 and 2 to the y coordinate of each particle. Stochastic generation of this value was meant to simulate not only flow from left to right but also dispersion. As can be seen the contaminant plume gradually moves away from the initial source zone becoming more diffuse with time especially at the leading edge.

A more likely scenario is that the contaminant source zone is not depleted in the short-to-medium term, but behaves as if there is a continuous injection of NAPL. In this case, plume development occurs, as simulated in Fig. 20.

As the diagram shows, the plume is most concentrated in the immediate vicinity of the source zone, but becomes dilute, as we move further away from the source zone. The rate of advective transport may be reduced by the partitioning of the organic NAPL component between the aqueous phase and organic matter attached to soil grains or rock in the sub-surface system. Basically, molecules attached to the solid phase are immobile. To calculate the fraction of immobile molecules, we need to be able to calculate the relative amounts of organic molecules in the aqueous and immobile organic matter phases. To do this, we need K_d the soil water distribution coefficient. K_d is a concentration ratio which we assume is constant under isothermal conditions and is described by the following equation:

$$K_d = \frac{[x]_{(soil)}}{[x]_{(aq)}}, \tag{34}$$

where the subscripts soil and aq refer to the concentrations of component x in soil and water, respectively. K_d is not particularly useful, since it is both soil and compound specific. However, we are able to provide an approximately compound specific parameter K_{oc}, where the subscript oc refers to the organic content present in the soil or rock sample. It is related to K_d by the following equation:

$$K_{oc} = \frac{K_d}{f_{oc}}, \tag{35}$$

where f_{oc} is the fraction of organic carbon in the soil or rock sample. The organic carbon content is the key location, where sparingly soluble organic compounds are adsorbed and/or absorbed in the sub-surface.

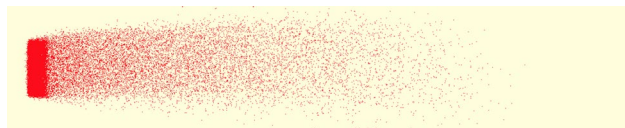K_{oc} values can be estimated using the following relationship [9]:

$$K_{oc} = 0.41 \cdot K_{ow}, \tag{36}$$
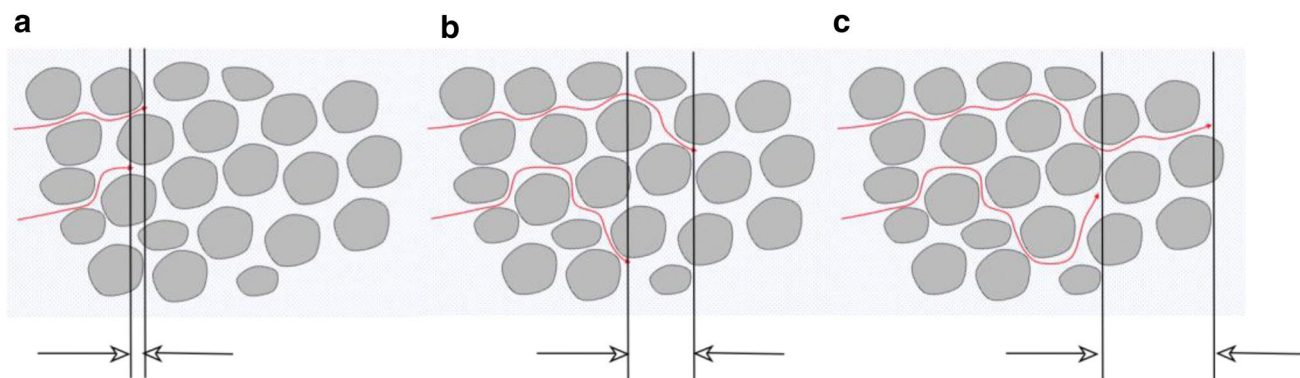
Fig. 18 Diagram showing how the amount of dispersion increases with the length the solute has travelled
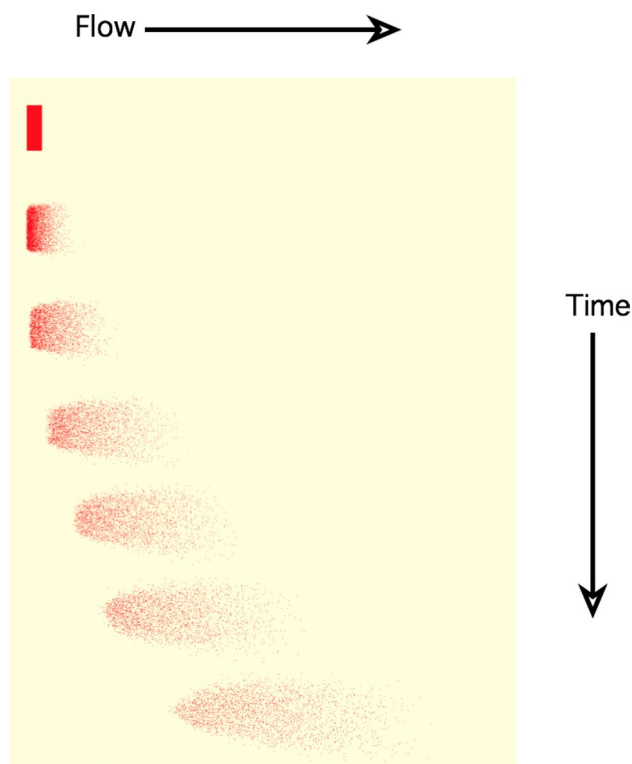
Flow ⟶

Fig. 19 Simulation of the dissolution of an NAPL component into flowing water and the subsequent development of a contaminant plume in the aqueous phase

Fig. 20 Plume development for the case of continuous injection of NAPL

where K_{ow} is the octanol water partition coefficient. Tables of K_{ow} values are widely available. It is now possible to estimate K_d using the following expression:
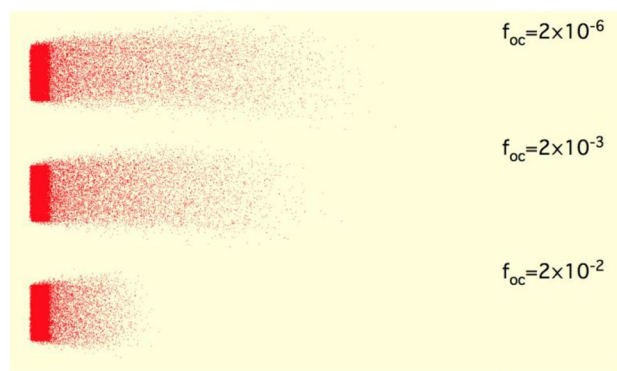
$$K_d = 0.41 \cdot K_{ow} \cdot f_{oc}. \tag{37}$$

The fraction of molecules attached to the solid phase (f_{solid}) is given by

$$f_{solid} = \frac{[x]_{(soil)}}{[x]_{(soil)} + [x]_{(aq)}}. \tag{38}$$

If we divide through $[x]_{(aq)}$, we obtain the following relationship:

$$f_{solid} = \frac{K_d}{1 + K_d}. \tag{39}$$

Fig. 21 Effect that increasing fraction of organic carbon has upon molecular transport

The term f_{solid} can be thought of as a probabilistic parameter which can tell us the probability that a particular molecule is attached to the solid phase. Thus, if we modify the advection dispersion and diffusion model used to generate Fig. 20 by generating stochastic values for the probability that a molecule is attached to the solid phase, then we can examine the impact of retardation upon plume development which is shown in Fig. 21.

Figure 21 was generated for benzene which has a K_{ow} value of $10^{2.13}$. The time over which each realisation was made is the same for the outputs in Figs. 20 and 21. Figure 21 shows the impact that increasing organic carbon fraction has on the retardation of the advective transport of the NAPL component.

It is normally found that there comes a point, where the mass transfer rate to the aqueous phase is balanced by the rate of dispersive transport away from the source zone. The net result is the establishment of a steady-state plume length.

Plume length can be attenuated by degradation. Many NAPL components provide food for sub-surface bacteria. If we assume that the degradation process is first order then we can write that the probability that a molecule will degrade in time, t, is

$$P(\text{degradation}) = \frac{[x]_0 - [x]_t}{[x]_0} = 1 - e^{-kt}. \tag{40}$$

The middle term is the fraction of material that has degraded in time, t. This can of course be directly interpreted as the probability that a molecule of component x will degrade in time, t. This interpretation allows us to stochastically generate numbers that simulate degradation. The term $[x]$ represents the concentration of component x. The subscripts refer to the concentration at time zero and time, t. k is the first-order degradation rate constant (units T^{-1}).

We can plainly see, in Fig. 22, that degradation reduces the size of the plume and that increasing degradation rate is associated with a greater reduction in the length of the

Increasing degradation rate

Fig. 22 Impact of degradation upon the size of the contaminant plume

plume. The time interval over which the realisations were made is the same as that used in Figs. 20 and 21.

Our assumption of first-order kinetics is critically dependent upon the assumption that the aqueous oxygen concentration (the obligate terminal electron acceptor in aerobic metabolism) is much greater than the concentration of the NAPL component. In practice, the amount of oxygen may be severely reduced—especially through losses brought about by the degradation process—and thus, the degradation rate may be much slower than anticipated. As we shall see in a subsequent manuscript dealing with the remediation and restoration of NAPL contaminated environments, the supplemental addition of oxygen or an oxygen release compound may be necessary to reduce the length of a contaminant plume to protect a public water supply well. This process is called bio-stimulation. The addition of bacteria that can aid the degradation is called bio-augmentation.

The term "terminal electron acceptor" requires further elaboration. All molecules used as a food source undergo oxidation to help in the production of the phosphorylating agent, ATP (adenosine triphosphate). The oxidation process involves the removal of electrons and hydrogen—in the form of protons—from the substrate. The electrons move along a pathway of interconnected protein complexes that act as both electron acceptors and donors. The complexes are physically arranged in the inner membrane of the mitochondrion—the cellular organelle, where these oxidation processes take place—in order of increasing redox potential, which is the order of decreasing free energy. The final step of the chain is the donation of an electron to a terminal electron acceptor. In aerobic metabolism, this is oxygen which has a large positive redox potential (indicating a high affinity for electrons). Under anoxic conditions (i.e., conditions, where oxygen is severely depleted or indeed absent) bacteria are able to use other terminal electron acceptors such as: NO_3^-, SO_4^{2-}, Fe^{3+}, and Mn^{4+}.

It is important to grasp that major NAPL releases of materials that are biodegradable results in rapid oxygen depletion in the vicinity of the release. Moreover, the subsequent use of other terminal electron acceptors may result in the release of metabolites that themselves are considered to environmentally harmful. For example, SO_4^{2-} reduction can lead

to the formation of hydrogen sulphide and NO_3^- reduction can lead to the formation of ammonia.

The advective transport of NAPL components in the vapour phase is driven by pressure gradients. Diffusion is often more important in the vapour phase than the liquid phase, because there are fewer intermolecular collisions. Dispersion occurs for the same reason, as it does in the aqueous phase. However, one feature that has an important impact upon vapour-phase transport is the presence of water in pores and pore throats. This water provides obstacles to the unrestricted movement of vapour and thus makes vapour transport pathways more labyrinthine or tortuous. The greater the degree of water saturation the greater the tortuosity of the pathway [9].

The presence of water additionally provides a mechanism for the retardation of vapour-phase components through absorption and adsorption. Absorption simply involves the aqueous dissolution of the organic component present in the vapour phase. In addition, NAPL components in the vapour phase are adsorbed to aqueous surfaces. The process results in a reduction of the surface tension of water which is thermodynamically favourable, since it results in a reduction in free energy.

NAPL fate and transport in the sub-surface: a summation

Figure 23 provides a conceptual overview of the fate of a DNAPL released into the sub-surface environment. NAPL released at ground surface migrates downwards in the unsaturated zone. Vertical downward transport is coupled with lateral spreading, as NAPL meets regions of capillary resistance. As the NAPL body migrates, residual droplets are detached from the trailing edge of the NAPL body and are held in pore spaces by capillary forces. In the unsaturated zone, components in the NAPL mixture are transferred to the vapour phase, via vaporisation.

The concentration (expressed as a partial pressure) of a contaminant component present in the NAPL phase is given by Raoult's law (Eq. 27). The contaminant molecules present in the vapour-phase migrate, because the vapour phase, as a whole, migrates in response to pressure gradients in the sub-surface atmosphere. This process is called advection. Vapour-phase migration is tortuous, since the vapour phase can only freely move through interconnected pore spaces that are not blocked by water. The greater the degree of water saturation in the unsaturated zone the greater the tortuosity of the transport pathway. Water also retards vapour-phase migration through adsorption and absorption and vapour transport is subject to dispersion. This occurs because of the numerous number of pathways available through the interconnected pore matrix. Some of these pathways are
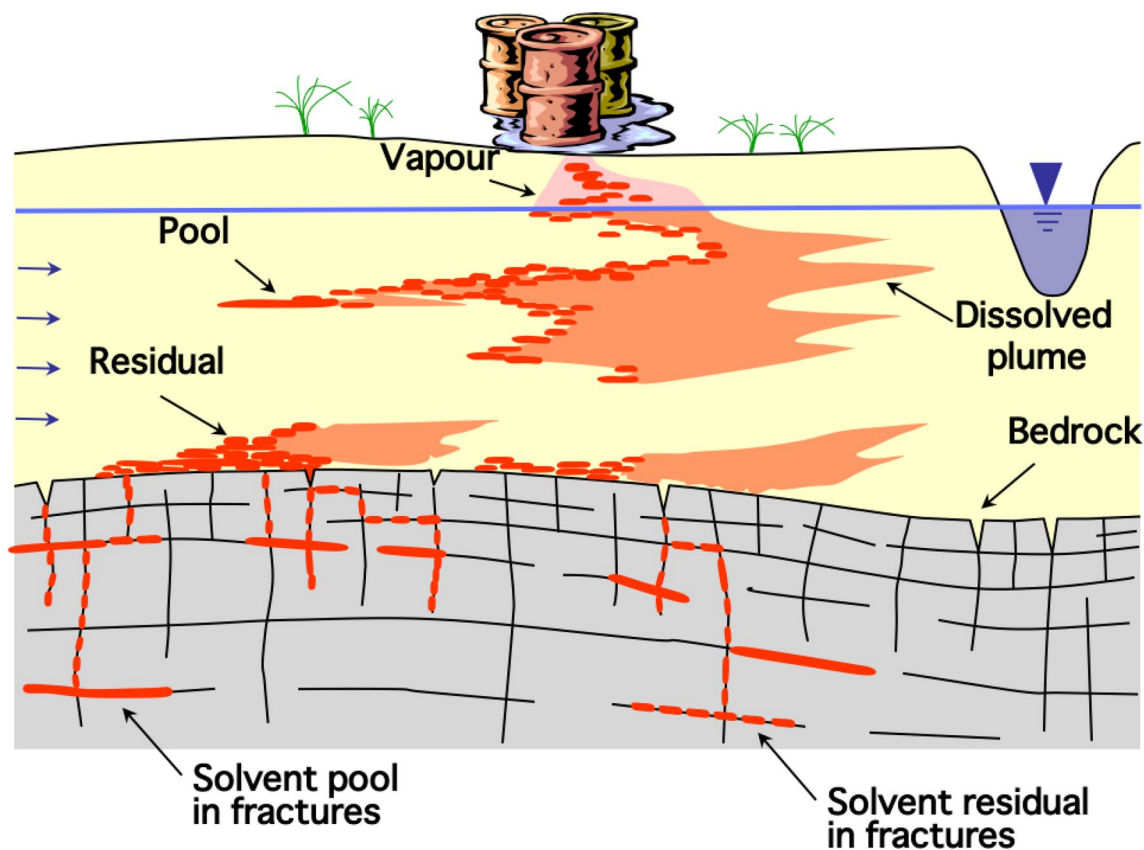
Fig. 23 Cartoon showing the fate of DNAPL in the sub-surface environment. The blue line represents the water table which is denoted by the blue inverted triangle symbol. The diagram is reproduced from reference [1]

relatively short some are relatively longer. This leads to a spreading out of the contaminant vapour plume emanating from the source zone, so that the leading edge of the plume is characterised by a much lower contaminant concentration than in the immediate vicinity of the source zone. Dispersion is also complemented by diffusion. Diffusion occurs because of molecular thermal energy.

Vapour-phase migration can be an important pathway through which a contaminant can be transferred from an NAPL source zone to a receptor. Very often, the receptor of most concern is human. The transfer of contaminants from the sub-surface environment to the indoor environment is of particular concern, since atmospheric contaminant levels can build up to levels considered hazardous to human health.

NAPL components present in the unsaturated zone dissolve in infiltrating rainwater which in turn leads to contamination of groundwater. Components present in LNAPLs that have accumulated at the water table and in DNAPLs that have migrated below the water table also dissolve directly into groundwater. Component concentration in groundwater in contact with the NAPL is given by a modification of Raoult's law (Eq. 30).

The steady dissolution of NAPL components produces a contaminant plume that is concentrated in the immediate vicinity of the NAPL source zone and becomes increasingly more dilute, as the plume moves further away from the source zone. At some stage, when the rate of dissolution is balanced by the rates of dispersion and degradation, the plume will attain a steady-state length. Once the source zone is depleted the plume length will shrink. From the point of view of an environmental practitioner, if the plume intersects a regulatory compliance point—such as a river or a public water supply well—then it becomes necessary to protect the at-risk receptors. This may be achieved by:

- reducing the source zone;
- enhancing the degradation rate of the contaminant components that comprise the plume;
- pumping contaminated water from the vicinity of the source zone and treating it to remove the contaminants;
- or hydraulically isolating the source zone.

Indeed, there is a plethora of techniques that have been proposed for dealing with NAPL contaminated groundwater. Risk assessment, groundwater restoration, and remediation

and the use of environmental forensics to ascribe liability for groundwater pollution will form the basis of a future second article.

DNAPLs that have sunk below the water table may eventually come into contact with bedrock. Here, the behaviour of the NAPL is determined by the nature of the rock. In many cases, NAPL will enter fractures and joints—breaks in the rock—because the entry pressure is relatively low. It should be noted that, as shown in Fig. 23, NAPL in vertical fractures will tend to form residuals trapped by capillary forces. NAPL in horizontal fractures may well accumulate to form potentially mobile pools. Whilst NAPL entry into rock fractures may be relatively straightforward, entry into the rock matrix maybe more difficult. Hard igneous rocks such as granite have very little if any primary porosity. Therefore, NAPL entry into igneous formations normally only occurs via the fracture network. Entry into sedimentary rocks that are composed of exceedingly tight pores—such as chalk—is also extremely unlikely. However, entry into the pore space of sedimentary rocks, such as the Permo-Triassic sandstone aquifer rocks in the UK, that have larger pores is possible and is dependent upon the head pressure exerted by the NAPL.

However, even if the NAPL cannot enter the surrounding rock, NAPL components can and do diffuse from the NAPL body into the surrounding porous medium, even if the pore structure is tight. This leads to a secondary problem: once the NAPL source zone has become depleted the contaminants will begin to back-diffuse from the porous rock back into the groundwater. Interestingly, the mass transfer of NAPL components to the surrounding rock medium does aid the retardation of a mobile NAPL body.

End words

The problems posed by NAPL contamination of the sub-surface are varied and complex. To be able to address these problems, it is important that the sub-surface geology is well characterised and that the chemical nature of the NAPL is well understood. How these goals can be achieved is site specific and the problems at individual sites are very often unique.

This manuscript has only dealt with the fate and transport of NAPLs in the sub-surface environment. A further manuscript is in preparation that will examine how we can deal with NAPL contaminated environments to sustainably remediate and restore them; how we can protect precious groundwater resources to be compliant with the EU's water framework directive; and how we can use chemical analysis to ascribe liability for NAPL spills to ensure that the polluter pays.

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Further reading

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