

From a draft being prepared by P. Jumars. Please do not cite without updates from <jumars@maine.edu>

## CHAPTER 2

### Jostling molecules and the edges of water

#### *No slip, surface tension and molecular diffusion*

*Brown, R. 1828. A Brief Account of Microscopical Observations Made in the Months of June, July and August 1827 on the Particles Contained in the Pollen of Plants; and on the General Existence of Active Molecules in Organic and Inorganic Bodies. Taylor, London.*

For analysis of macroscopic flows, water legitimately is treated as a continuous medium. A cubic centimeter of liquid water contains about  $3.34 \times 10^{22}$  molecules, so individual molecular speeds and directions in its interior can hardly be expected to contribute to its bulk movement: They average out. Numbers this large are difficult to conceive. If you could build a device to count one billion of these water molecules per second, it would take over a million years to count the total. Nevertheless, boundaries are often nearby in such a small volume, and biologists inevitably are interested in the interactions of water with solid boundaries, *i.e.*, exterior and interior surfaces of organisms. The typical laboratory setting moreover involves a greater air-water interfacial area per unit of volume of water than does the typical field environment, so being aware of the physical effects of interfaces is of some importance in avoiding incorrect field inference from laboratory observation. Behavior of flows at these solid-liquid or liquid-gas interfaces cannot be as omnidirectional as in the bulk at either the macroscopic or the microscopic scale.

Understanding some aspects of flows at interfaces and of fundamental differences between mass and momentum transfer — even in the fluid interior — requires appreciation for the spacings, movements and interactions of molecules. Natural waters are dilute media for constituents other than water, so a great deal of the physical transport behavior of dissolved substances, such as nutrient molecules taken up by bacteria and phytoplankton, can be understood from the behavior of water molecules.

Mean kinetic energy of a molecule over time or across a large group of molecules at any one time (the term on the far left) and thermodynamic temperature,  $T$ , are linked in the definition of  $T$ :

$$\left\langle \frac{m\mathbf{u}^2}{2} \right\rangle = \frac{m\langle \mathbf{u}^2 \rangle}{2} = \frac{3k_B T}{2}, \quad (2.1)$$

where  $m$  is the mass of the molecule and  $k_B$  is the Boltzmann's constant ( $1.38054 \times 10^{-23}$  J K<sup>-1</sup>). Root mean square speed,  $\sqrt{\langle \mathbf{u}^2 \rangle}$ , is a useful measure of the spread of speeds among molecules and also increases with temperature and decreases with molecular mass in a manner that is easily seen by rearranging Eq. 1.1. Mean speed,  $\langle u \rangle$ , of a molecule is only slightly more difficult to calculate:

$$\langle u \rangle = \sqrt{\frac{8k_B T}{\pi m}}. \quad (2.2)$$

As temperature rises, both mean speed and the spread of the distribution of speeds increase, and those molecules that chance both to have sufficient speed and to be close enough to the water surface and heading in the right direction will leave — evaporate.

These mean kinetic energies and speeds are true of all matter in thermodynamic equilibrium, independent of phase, but molecules of solids maintain predictable structure over many molecular diameters (knowing the position of one molecule or atom allowing prediction of the locations of neighbors), and molecules are so closely packed that the position of a molecule everywhere else except at the surface of the solid is essentially fixed. Hence the thermal motion is generally described as a vibration within the cage formed by neighboring molecules. In the atmosphere, molecules fly 10 or 100 molecular diameters before hitting a neighbor and transferring some momentum. In a liquid, molecules are not quite close packed, but neighbors are on average less than one molecular radius apart, order or structure generally extends no more than a few molecules away at any one instant, and molecular positions are not maintained over time. The world in a gas or liquid at this molecular scale is both violent and stochastic. According to Eq. 1.2, a water molecule at room temperature (20°C) will be traveling on average at 587 m s<sup>-1</sup>, faster than sound in air and far faster than any organized flow of natural waters. Any given molecule in the water's interior will be bombarded from all directions at high speeds.

Water molecules are roughly 0.32 nm in diameter. The number cannot be more precise because the molecule is not spherical, but has two hydrogen “ears” projecting from one oxygen atom. People who work on molecules prefer to use the angstrom unit, Å, which is 10<sup>-10</sup> m because, despite the much larger variation in the mass per atom in the periodic table, the range in diameters of a single atom is very small, only 1 - 5 Å. In the most common form of ice, hexagonal crystals have unit cell dimensions of 4.51 × 7.35 Å. Water is a curious substance in many ways. One is that the molecules in liquid state are on average somewhat *closer* together than in the solid — at an average separation of 3.7 Å. Hydrogen bonding is key in explaining the sparse packing of ice crystals, but it is also responsible for some degree of order in the liquid phase and for the high viscosity of a liquid having such a small molecule. Temperature effects on hydrogen bonding are also responsible for the large (roughly two-fold) change in dynamic viscosity of liquid water over the range of its common environmental temperatures (0 - 40°C). Dynamic viscosity is the internal frictional resistance of the fluid to deformation. I will get more accurate and precise about its definition shortly. Substantial evidence indicates that liquid water molecules occur with some statistical regularity in 280-molecule, 3-nm diameter, icosahedral clusters. The hydrogen bonds in liquid water, however, are constantly breaking and reforming as individual molecules swing about their hydrogen bonds with neighbors and collide. Nevertheless, there is more long-range order and hence more resistance to flow than in a more typical liquid with a small molecule that does not engage in hydrogen bonding.



**Fig. 1.1** Wettability of a surface, illustrated by the angle that a small, liquid drop makes with that surface. The angle is always measured inside the droplet. The more wettable the surface by the liquid, the smaller the contact angle,  $\theta_c$ , so that the surface in **A** is more wettable by the respective liquid than the surface in **B**.

At the scale of individual molecules, surfaces cannot be perfectly smooth. If molecules were ball bearings, in a flow over a solid they would be rolling over a layer of glued-down ball bearings. Moreover, to extend the metaphor, they are magnetized; there are charge attractions between molecules of water and the surface. Particularly the first two layers of water molecules over the solid are more tightly bound, usually oriented with their “Mickey Mouse ears” of hydrogen pointing toward the typically negatively charged solid. This bilayer, in turn, interacts more weakly with adjacent water molecules, which prefer, in a statistical sense, to aggregate into 3-nm icosahedra. Out to 3 nm from the surface or beyond, then, the water is more resistant to movement than it is in the bulk. For all but some very unusual conditions outside of ordinary environmental experience, more than a century of research has shown that the closest layer of water to a solid boundary has the same velocity as that solid boundary, no matter the wettability of the boundary. This result is called the “no-slip” condition.

Although the first layer of water will not slip, adhesive strength of water to surfaces varies with the chemical properties of the surface. Surfaces comprising polar molecules are in general more “wetable,” that is, water adheres more strongly to them than to non-polar surfaces. A very simple test of how strongly water adheres to a solid versus to itself is to put a small drop of water on the surface (Fig. 2.1), and the result will be very familiar from observations of water droplets on waxed surfaces such as waxed paper and leaves of many plant species, which “bead” (are not very wettable). Most natural surfaces are wettable, but some crustacean cuticles are very non-wettable or hydrophobic. Similar effects are pronounced in insects that walk or float on the water surface (*e.g.*, water striders and whirligig beetles). The “snorkel” in the tail of a mosquito larva can be rotated to present either a hydrophobic or hydrophylic surface depending on whether the larva is at the surface to breathe or submerging to feed or evade. It is easy to forget when talking about wettability that three phases (including the gas) are involved, as some thinking about these examples will help to reveal. That is, absent a gas-liquid boundary, the surface has been fully wetted, and the liquid closest to the solid does not slip.

Much of the droplet behavior on a surface arises from the fact that forces are asymmetric on molecules near the gas-water interface. Because there is a much more rarified fluid on the gas side of water molecules at the interface and because most gas molecules are less polar than water, liquid water molecules at the interface are pulled only weakly by the gas molecules. The net effect of this anisotropy is a

tension along the water surface, analogous to the forces in a stretched rubber film. In the case of water droplets, the liquid inside the film is incompressible (cannot change volume except by evaporation), so the air-water interface will be pulled toward a spherical geometry. The strength of this effect is quantified as surface tension,  $\gamma$  [ $\text{M T}^{-2}$ ], which for water is isotropic along the surface. As is often the case, these dimensions make more intuitive sense in a less reduced form. That is, a surface tension is literally a force per unit of distance [ $\text{M L T}^{-2} \text{L}^{-1}$ ], required to stretch the surface over that distance. The dimensions reflect the fact that the work ( $W$ ) involved in forming additional surface area ( $S$ ) is proportional, through the surface tension,  $\gamma$ , to the area of the surface formed,

$$dW = \gamma dS. \quad (2.3)$$

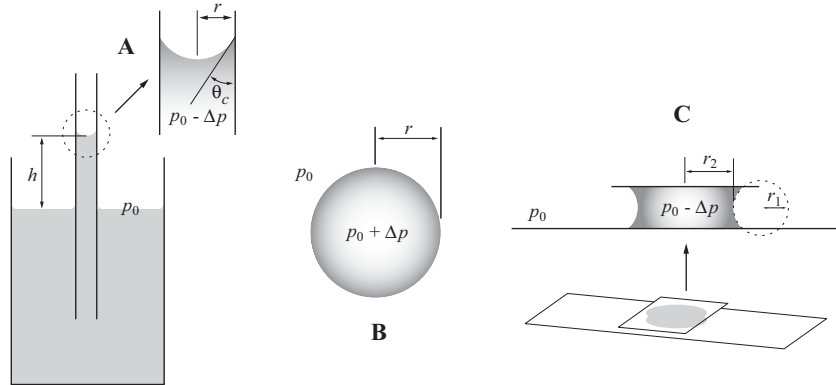
The work needed to increase surface area accounts for circular shape of the air-water interface in cross section in Fig. 2.1 and in many other settings. Any interface shape that departed from a segment of a sphere would require more work. I recommend Denny (1993) to readers interested in further details and derivations for problems involving surface tension. I will simply use a few of his results to continue developing a geometry that I will revisit frequently, *i.e.*, that of two flat plates, with one stationary and the other sliding over it. What is happening in this setting is easier to understand, however, by visiting a more familiar example first, that of a meniscus in a liquid. This visit is also a chance to review or introduce some other properties of water. Hydrostatic pressure,  $p$  [ $\text{M L}^{-1} \text{T}^{-2}$ ] is a force per unit of area, *i.e.*, a stress, and is the same in every direction. Hence it requires no vector notation, but at any surface it will push orthogonally on that surface, so it applies an inward normal stress,  $-\sigma_i$  on the object. Hydrostatic pressure under a column of water  $h$  [L] units deep is

$$\Delta p = \rho gh, \quad (2.4)$$

where  $\rho$  is fluid density [ $\text{M L}^{-3}$ ],  $g$  is the acceleration due to gravity [ $\text{L T}^{-2}$ ], and  $\Delta p$  indicates the difference between ambient pressure at the water surface and the pressure under the column of height  $h$ . A difference in a quantity carries the same dimensions as the quantity itself.

Mercury in a vertical glass cylinder is an example of a liquid that shows greater cohesion (pull of the liquid on itself) than adhesion to the glass. Water, on the other hand, shows greater adhesion to glass than cohesion. Glass is more wettable by water than it is by mercury. Hence the meniscus in a tube of mercury is convex upward, while that of water is concave upward. Therefore surface tension pulls a column of mercury downward, whereas it pulls a column of water upward (Fig. 2.2A). The height,  $h$ , [L] to which the water column will be drawn above the ambient water level is (Denny 1993, p. 259)

$$h = \frac{2\gamma \cos \theta_c}{r\rho g}. \quad (2.5)$$



**Fig. 1.2** Common geometries in which surface tension affects pressure. **(A)** Capillarity pulls a column of water upward to height  $h$  in a glass tube. Just below the meniscus, pressure is below ambient ( $< p_0$ ). **(B)** A droplet or bubble of one fluid inside another has its internal pressure raised above ambient external pressure. **(C)** A droplet of water under a microscope coverslip takes on a squat, columnar shape with two characteristic radii. The curvature indicated by  $r_2$  is concave inward, raising the pressure in the water, whereas the curvature indicated by  $r_1$  is convex inward, lowering the internal pressure. Typically  $r_1 \ll r_2$ , so the coverslip is pulled quite strongly toward the slide by fluid at  $p < p_0$ .

Here  $r$  is the radius of the tube; note that the height to which water will rise is inversely proportional to the radius of the tube. It is worth remembering that the lower pressure in a surface-tension problem is on the convex side. Surface tension is pulling water up, reducing pressure below the affected interface.

Another common geometry that we will revisit is that of a spherical droplet or bubble of fluid in another fluid (*e.g.*, of air under water). Again the higher pressure will be on the concave side, or inside a droplet or bubble (Fig. 2.2B, and

$$\Delta p = \frac{4\gamma}{r}, \tag{2.6}$$

where  $r$  is the radius of the bubble or droplet and  $\Delta p$  is the difference between pressure outside and inside this sphere. For small droplets or bubbles, the interior pressure can be substantial. For example for a bubble of  $50 \mu\text{m}$  radius, taking  $\gamma = 0.07 \text{ Newton m}^{-1}$  (which is accurate to this level of precision at all common environmental temperatures of liquid fresh water of  $0$  to  $40^\circ\text{C}$  and for seawater in the portion of that range  $> 10^\circ\text{C}$ ),  $\Delta p = 3 \times 10^3 \text{ Pa}$ !

The last common geometry is one with which most introductory biology students have dealt in looking through a microscope at a drop of water under a coverslip (Fig. 2.2C). Here (Denny 1993),

$$\Delta p = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right), \tag{2.7}$$

where  $r_1$  and  $r_2$  have the linear dimensions indicated in Fig. 2.2C.

This latter geometry is also one that will help to review the properties of water layers of varying thickness. The forces of interest are those required to pull one flat plate over the other tangentially, like dragging a book horizontally along a desktop by a string attached to one end or pulling the coverslip over the slide's surface. Nanotechnology recently has enabled this experiment on very small specimens of silicon wafers, and the results have confirmed long-standing theories about the organization of water molecules at interfaces (Serge and Gorb 2001).

It is difficult to get all the water off of hydrophylic surfaces and doing so may require a partial vacuum. In dry, sliding friction of macroscopic objects, a simple formula generally serves to describe the force required to keep the object moving at a fixed speed:

$$\mathbf{F}_f = k_f \mathbf{F}_n . \quad (2.8)$$

$F_f$  is the frictional force,  $k_f$  is a friction coefficient characteristic of the two materials (one in our case of smooth glass), and  $F_n$  is the net force normal to the surfaces that is pushing the coverslip and glass plate together. If one applies no tangential force at the outset but ramps it up, a characteristic of solids in contact is that they show "stick-slips," episodes in which asperities or stochastic alignments of force fields of molecules cause sticking until the force builds sufficiently to overcome the resistance, and the surfaces slip. In the example, the tiny weight of the coverslip pressing down on the plate and the smooth surfaces will make the forces required to initiate or maintain sliding very small for a truly dry coverslip. Nevertheless, allowing a monolayer of water to form (*e.g.*, by decreasing the vacuum) reduces the force required to initiate or maintain movement. When two to three monolayers worth of water separate the smooth solid, stick-slips become periodic rather than stochastic when the velocity at which the plate is pulled is small: The bilayer structure is disrupted and reforms. Viscosity is measurably larger than for thicker layers of water, again reflecting this resistance to deformation from the most stable molecular configuration. No such stick-slips are observed above a three-monolayer thickness of water, where capillarity becomes dominant (*cf.* Fig. 2.2C, until the scales of separation approach 1 cm). The negative pressure inside the capillary bridge or column adds to the weight of the coverslip, effectively increasing  $F_n$ .

I have been careful to discuss a geometry in which solid surfaces are parallel. When lubrication is the aim, that geometry is often discarded in favor of one that forces fluid into a narrowing gap, thereby raising fluid pressure and reducing  $F_n$ , quite the opposite of Fig. 2.2C. This effect is apparent to anyone who has slid a piece of paper across the table or has taken a successful jump onto a piece of plywood in the swash zone of a beach. It is also the principle behind lubrication of eccentric shafts in journal bearings, such as those in automobile engines. I will not be returning to this topic in any systematic way, although it {lubrication theory} is a subdiscipline quite closely related to topics covered here. Lubrication theory and applications make extensive use of one of the fundamental properties of flows at low Reynolds numbers, *i.e.*, their abilities to produce and support high pressures.

Mean tangential velocities of water molecules match mean velocities of the surface, even in the case of lubricants. Lubrication does not produce slip, but

instead generates pressure that opposes the forces bringing solid surfaces together. The no-slip condition, then, makes advection along a surface ineffectual at bringing molecules all the way to the surface, and it is time to return to the role of molecular motions in momentum and mass transport both to and from surfaces as well as within the interior of a stagnant fluid. Momentum can be transferred through the pack of molecules by successive collisions — without the need for a single molecule to carry it all the way. Mass transfer, on the other hand, requires moving the molecule all the way through the pack. When the cue ball hits the assembled group of billiard balls, momentum gets transferred effectively, but the white cue ball does not penetrate the pack very far. Hence you should expect and will find that in fluids — but especially in nearly close-packed liquids — momentum is transferred by molecular motions much more effectively than is mass.

People are used to traveling at roughly constant speed and maintaining direction (*i.e.*, moving at constant velocity). On average, it takes us twice as long to go twice as far. In the molecular world of bumper cars, however, these rules do not apply. Average speed is maintained or resumed so long as temperature remains constant, but directions change with each collision. Absent an organized flow, what is the best guess of the location of a water molecule relative to its point of release (which we can make the origin of the Cartesian or spherical coordinate system), after some time interval,  $t$ , has passed? It is the release point, because direction is effectively randomized. Although true, this answer is misleading. On average it will be farther from the origin with increasing  $t$ , but in what direction? Any one direction is an equally good guess, but how far?

Although the molecule will indeed have moved on average 587 m in one second, its starting and ending points will on average be separated by much less than 587 m. A good intuition for how far it will go can be gained by some simple two-dimensional simulations on graph paper or on a computer by moves on a grid, with equal probability in each time step of moving one step left, right, up or down. {1D, 2D, or 3D random walk model}. What you will find is that unlike the situation of moving in a straight line, the square of the distance,  $l$ , to the point of release or origin increases linearly with time:

$$\frac{l^2}{t} = \text{constant} . \quad (2.9)$$

Water is very effective at randomizing the motions of its own or dissolved chemical molecules. The average distance between water molecules is  $0.5 \text{ \AA}$ , so at the mean velocity a water molecule will have about  $1.2 \times 10^{13}$  collisions (steps in a random walk) per second. For that reason, despite the high speed, net progress in a given direction, and hence this constant, are both small. The process of such movement fueled by thermal energy of molecules is aptly called molecular diffusion.

Eq. 2.9 is not quite conventional. Because in random motion only one-half of the steps are effective at increasing net distance moved (the other half closing the distance to the starting point), a more mechanistic and consistent derivation yields

$$\frac{l^2}{2t} = D. \quad (2.10)$$

Clear derivations are easily accessed (Berg 1983; Denny 1993), and Cussler (1997) provides deep physical insight into the process and consequences of diffusion, so I will strictly limit my introduction to the manipulation of Eq. 2.10 in simple but general circumstances. You already know the dimensions that this constant,  $D$ , must have. Because the left side of the equation has dimensions  $[\text{L}^2 \text{T}^{-1}]$ , so must  $D$ , which is known as the (molecular) diffusion coefficient for a substance. In turn because most collisions will be with water, most small molecules dissolved at low concentrations in water — and water itself — have very similar values of  $D$  near  $1 \times$  or  $2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  ( $1 \times$  or  $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).

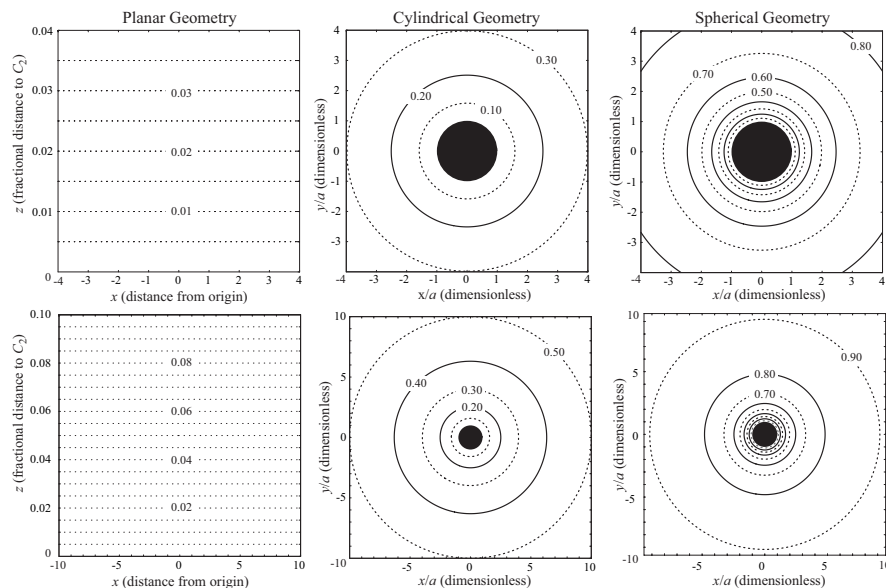
Equation 2.10 is more profound biologically than its simple structure might suggest. Rearranging to calculate how long on average it will take a molecule to diffuse a given straight-line distance (although the molecule will not follow a straight path to cover that distance),  $t = l^2/2D$ . Don't hold your breath to calculate the implications for real organisms, because you are too large to live by supplying your oxygen by molecular diffusion alone. Let's choose oxygen, then, which in water at  $20^\circ\text{C}$  has  $D = 1.97 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . The time to diffuse  $1 \mu\text{m}$  is only 0.25 ms, but the time to diffuse 1 m (roughly the scale from your air intake to the extremes of your body) is 8 yr! It thus is apparent why animals bigger than 1 mm in size have some kind of circulation (advection) system to move oxygen.

Systems head for maximum entropy, and the eventual system result of this intense, diffusive, molecular jiggling in a solution is to eliminate concentration differences above the molecular scale by driving water molecules into above-average solute concentrations and driving solute molecules out. At any one time, many water and solute molecules are moving opposite to this trend, but the net result that becomes evident at the scales of most concern to this book is that solutes are transported by molecular diffusion from areas of high concentration to areas of low, following Fick's first law:

$$\mathbf{J}_z = -D \frac{\partial C}{\partial z}, \quad (2.11)$$

where  $\mathbf{J}_z$  is the flux of solute in the  $z$  direction, and  $C$  is the concentration  $[\text{N L}^{-3}]$  of solute. Numbers of molecules are generally measured in moles, where one mole is Avogadro's number ( $6.02 \times 10^{23}$ ) of atoms, molecules or ions. You may have learned concentrations with dimensions of  $[\text{M L}^{-3}]$ , and it is perfectly feasible to convert between the two by knowing the mass per mole of the molecule. The physics and chemistry in this book, however, have a decidedly biological focus, and it is much easier to connect moles than weights to studies of physiological transport and uptake.

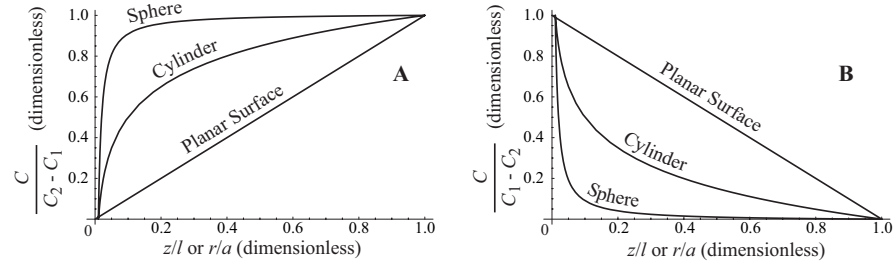
Flux is a critical concept for the major topics of this book, and so it is important to understand its meaning from the outset. A good start is with the dimensions of  $\mathbf{J}_z$ . Dimensions of the three variables on the right, respectively, are  $[\text{L}^2 \text{T}^{-1}]$ ,  $[\text{N L}^{-3}]$  and  $[\text{L}^{-1}]$  (as  $z$ , a length scale, is in the denominator). Multiplying



**Fig. 1.3** Steady-state diffusion in simple geometries of one to three dimensions, with a low surface concentration  $C_1$  at  $z = 0$  for the planar geometry and  $r = a$  for the other two geometries. Isolines in each case plot  $C/(C_2 - C_1)$ , as the concentration increases toward  $C_2$  at any distance for the planar geometry and at  $r = 100a$  for the other two geometries.

gives dimensions for  $J_z$  of  $[N L^{-2} T^{-1}]$  or moles per unit of area per unit of time. Geometry is important; the area of concern here is perpendicular to the  $z$  direction. Eq. 1.5 is written as a partial derivative and is valid in any case, *e.g.*, even when concentration also changes in the other two directions,  $x$  and  $y$ . If the only concentration gradient is in the  $z$  direction, or if we rotate the coordinate system so that  $z$  is in the direction of the gradient, we can write the gradient in concentration as a total derivative,  $dC/dz$ . The negative sign in Eq. 1.5 assures a match to the observation that net molecular diffusion operates to reduce order inherent in the gradient, *i.e.*, to move material from high concentration to low.

Biological diffusion questions often occur in one of the three simple geometries, and they provide an early reason to adopt an onion- or Russian doll-resembling geometry of layers covering these three geometries. The simplest case that can be compared across all three geometries is of a surface maintained at some concentration,  $C_1$ , with the concentration at some distance  $z$  from the flat surface or  $r/a$  from the cylinder or sphere maintained at some different concentration,  $C_2$ . The formulas that I adapt from Crank (1975) can be used for any values of  $C_1$  and  $C_2$ , but I illustrate specifically the case (Fig. 2.3) wherein the surface at which  $C_1$  is measured is a sink, *i.e.*, is taking up the solute at the rate at which diffusion is supplying it. For the steady-state solutions, between the surfaces where concentrations are set, the same flux must be crossing successive  $x$ - $y$  planes of height  $z$  and successive surfaces at  $r/a$  from the cylinder's or sphere's surface.



**Fig. 1.4** Concentration versus distance from a source or sink in the three simple geometries of Fig. 1.3. **A.** The surface at  $z = 0$  or  $r = a$  is a sink ( $C_1 < C_2$ ). **B.** The surface at  $z = 0$  or  $r = a$  is a source ( $C_1 > C_2$ ). The curves are direct reflections of the way that volume in which diffusion operates varies with distance  $z$  from the surface: In a planar geometry volume of the system increases linearly with distance  $z$  from the surface. In a cylindrical geometry, volume increases as  $r^2$  with distance  $r$  from the surface, whereas for the sphere it increases as  $r^3$ . Steepness of the gradient at the surface determines flux per unit of area, which arrays as sphere > cylinder > planar surface.

In the case of the planar surface, each successive plane upward from the surface has the same area, so the concentration gradient at each plane must be the same if the flux is to remain constant. That is, the concentration gradient must be linear between  $C_1$  and  $C_2$ . Setting the origin ( $z = 0$ ) as the point where  $C = C_1$  and  $l$  as the distance between the planes where  $C = C_1$  and  $C = C_2$ , respectively, gives

$$C(z) = \frac{C_1 - C_1 z + C_2 z}{l}. \quad (2.12)$$

A constant gradient cannot hold for the other geometries at steady state: Successive cylindrical shells increase in surface area with  $r$ , just as does the circumference of a circle, whereas successive spherical shells increase in surface area as  $r^2$ . To maintain constant flux, the gradient in concentration must therefore vary as  $1/\ln r$  and  $1/r$  for the cylinder and the sphere, respectively, if the flux between  $C_1$  and  $C_2$  is to remain constant. Specifically, for a cylindrical geometry,

$$C(r) = \frac{C_1 \ln \frac{b}{r} + C_2 \ln \frac{r}{a}}{\ln \frac{b}{a}}, \quad (2.13)$$

whereas for the spherical geometry,

$$C(r) = \frac{aC_1(b-r) + bC_2(r-a)}{r(b-a)}. \quad (2.14)$$

For both these geometries  $r$  is radial distance from the center of the cylinder or sphere,  $a$  is the cylinder or sphere's radius and the surface on which  $C = C_1$ , and  $b$  is the radial distance at which the concentration rises or falls to  $C_2$ .