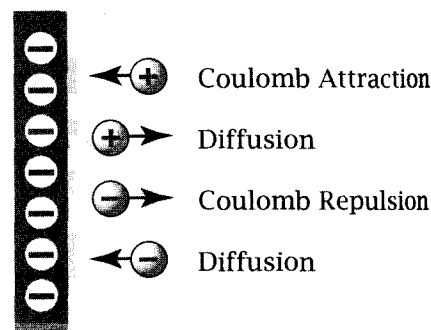


**Figure 23.1** Dissociated mobile salt ions move in the presence of a charged surface. The counterions are attracted to the surface and the co-ions are repelled.



present. The electrostatic interactions of a charged object with added salt can be described by the Poisson equation, and its equilibrium is described by the Boltzmann distribution law. Combining these gives the Poisson-Boltzmann equation.

### The Poisson-Boltzmann Model for the Distribution of Mobile Salt Ions Around Charged Objects

A charged molecule or surface  $P$  attracts the mobile salt ions that have the opposite charge to  $P$ , called the *counterions*.  $P$  repels the mobile ions of the same sign, called the *co-ions* (see Figure 23.1). The counterions distribute around  $P$  and act as a sort of electrostatic shield, reducing the electrostatic potential that is felt by a particle more distant from  $P$ . The interface between  $P$  and the neighboring salt solution is called the *electrical double layer*: the first layer is the charge on  $P$ , and the second layer is the adjacent diffuse sea of excess counterions.

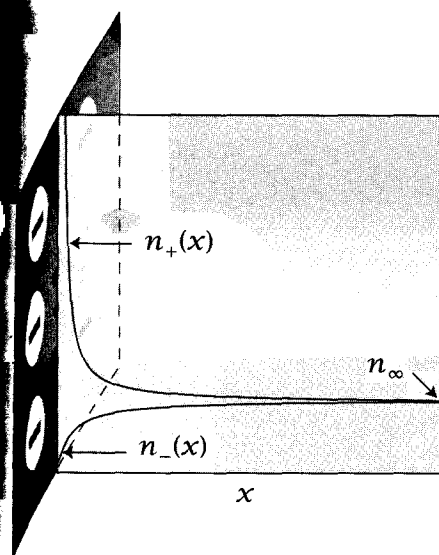
In the absence of electrolyte, two negatively charged  $P$  particles repel each other. But if a salt such as NaCl is added to the solution, the small ions intervene to weaken the charge repulsions between the two negative  $P$  particles, often to the point that other weak attractions can prevail and cause the  $P$  particles to associate. In this way charged colloids can be induced to aggregate by the addition of salts.

River deltas are interesting cases of electrostatic shielding, for example where the Mississippi River meets the ocean. In the upstream fresh river water, fine silt particles are suspended, owing to soil erosion from the surrounding land. Silt particles are charged colloids. The fresh water carries the silt downstream toward the ocean. Where the fresh water meets the salty seawater, the high salt concentration causes the colloidal silt to aggregate and precipitate to form the macroscopic landforms known as deltas.

The simplest model of charge shielding and colloidal stability against aggregation was developed around 1910 independently by L-G Gouy (1854-1926), a French physicist, and DL Chapman (1869-1958), a British chemist. They combined Poisson's equation of electrostatics with the Boltzmann distribution law.

In the simplest case, the surface of a charged colloidal particle is described as a plane. Suppose that a charged  $P$  particle, which is fixed in space, produces an electrostatic potential  $\psi(x)$ , which you take to be a function of a single spatial coordinate  $x$ .  $P$  is in a salt solution of dissociated mobile ions. Let

**Figure 23.2** The concentration of counterions  $n_+(x)$ , and concentration of co-ions  $n_-(x)$  as a function of distance  $x$  away from a negatively charged surface.



$n_+(x)$  represent the concentration of mobile positive ions (the number of ions per unit volume) at a distance  $x$  from the plane. This quantity is given by the Nernst or Boltzmann equation (22.8),

$$n_+(x) = n_\infty e^{-ze\psi(x)/kT}, \quad (23.1)$$

where  $n_\infty$  is the concentration of positive ions in the bulk solution, distant from the particle  $P$ , where the potential is  $\psi(\infty) = 0$  (see Figure 23.2). An identical expression applies to the negative ions, except that  $z$  is replaced by  $-z$ , if the electrolyte is symmetrical in its charge. Charge neutrality in the bulk requires that the number density of negative ions in the bulk far away from  $P$  is also  $n_\infty$ , so

$$n_-(x) = n_\infty e^{+ze\psi(x)/kT}. \quad (23.2)$$

The mobile ions not only *experience* the electrostatic field from  $P$ . They also *contribute to it*. You can compute the electrostatic potential that arises from both the fixed charge from  $P$  and from the mobile charges of the dissociated salt ions. First, compute the total charge density  $\rho(x)$  as a function of the number of ions at position  $x$ :

$$\rho(x) = \sum_i z_i e n_i(x) = ze [n_+(x) - n_-(x)], \quad (23.3)$$

where  $z_i$  is the valence of an ion of species  $i$ , and  $n_i$  is its concentration at position  $x$ . Now use the Poisson equation (21.30) to relate the charge density  $\rho$  to the electrostatic potential  $\psi$ :

$$\nabla^2 \psi = -\frac{\rho}{D\epsilon_0},$$

where  $D$  is the dielectric constant of the solution.  $D$  is approximately equal to the dielectric constant of the solvent, because the ions themselves (if their concentration is low) contribute little to  $D$ .

**Table 23.1** The Debye length  $1/\kappa$  describes the range of the potential, given here for various concentrations  $c$  of aqueous monovalent salt solutions at 25 °C.

| $c$<br>(mol L <sup>-1</sup> ) | $1/\kappa$<br>Å |
|-------------------------------|-----------------|
| 0.5                           | 4.30            |
| 0.2                           | 6.80            |
| 0.1                           | 9.62            |
| 0.05                          | 13.6            |
| 0.02                          | 21.5            |
| 0.01                          | 30.4            |
| 0.005                         | 43.0            |
| 0.002                         | 68.0            |
| 0.001                         | 96.2            |

Now you have all the terms necessary to formulate the **Poisson–Boltzmann equation**. Substitute  $n_+(x)$  and  $n_-(x)$  from Equations (23.1) and (23.2) into Equation (23.3) for  $\rho$  and then into Equation (21.30):

$$\nabla^2\psi = \frac{ze n_\infty}{D\epsilon_0} (e^{ze\psi/kT} - e^{-ze\psi/kT}). \quad (23.4)$$

Equation (23.4) can be expressed more compactly in terms of the hyperbolic sine function,  $\sinh(x) = (e^x - e^{-x})/2$ :

$$\nabla^2\psi = \frac{2ze n_\infty}{D\epsilon_0} \sinh(ze\psi/kT). \quad (23.5)$$

The Poisson–Boltzmann equation (23.5) is a nonlinear second-order differential equation from which you can compute  $\psi$  if you know the charge density on  $P$  and the bulk salt concentration,  $n_\infty$ . This equation can be solved numerically by a computer. However, a linear approximation, which is easy to solve without a computer, applies when the electrostatic potential is small. For small potentials,  $ze\psi/kT \ll 1$ , you can use the approximation  $\sinh(x) \approx [(1+x) - (1-x)]/2 = x$  (which is the first term of the Taylor series expansion for the two exponentials in  $\sinh(x)$  (see Appendix C, Equation (C.1)). Then Equation (23.5) becomes

$$\nabla^2\psi = \frac{2ze n_\infty}{D\epsilon_0} (ze\psi/kT) = \kappa^2\psi, \quad (23.6)$$

where  $\kappa^2$  is defined by

$$\kappa^2 = \frac{2z^2 e^2 n_\infty}{D\epsilon_0 kT}. \quad (23.7)$$

Equation (23.6) is called either the **linearized Poisson–Boltzmann** or the **Debye–Hückel equation**.  $1/\kappa$  is called the **Debye length**. The Debye length is a screening, or shielding, distance. A charge that is closer to  $P$  than  $1/\kappa$  ‘sees’ the charged plane and interacts with it. A charge that is further than  $1/\kappa$  from  $P$  is shielded from it by the intervening salt solution, which weakens its attraction or repulsion for the plane. Table 23.1 shows that increasing the concentration of the salt decreases the Debye length. Example 23.1 shows how the Debye length is computed.

**EXAMPLE 23.1 Computing Debye lengths.** For a monovalent salt,  $z = 1$ , with concentration 0.1 mol L<sup>-1</sup>, show that the Debye length is 9.62 Å if  $D = 78.54$  (see Table 23.1).

Multiply the numerator and denominator on the right-hand side of Equation (23.7) by Avogadro’s number  $\mathcal{N}$  to get

$$\kappa^2 = \frac{2(ze)^2 n_\infty \mathcal{N}}{D\epsilon_0 RT}.$$

From the units given in the box on page 370,  $e^2 \mathcal{N}/(4\pi\epsilon_0) = 1.386 \times 10^{-4} \text{ J m mol}^{-1}$ , so

$$\kappa^2 = 2(4\pi) (1.386 \times 10^{-4} \text{ J m mol}^{-1}) (0.1 \text{ mol L}^{-1}) (10^3 \text{ L m}^{-3})$$