

# **Kinetic Properties of Colloids**

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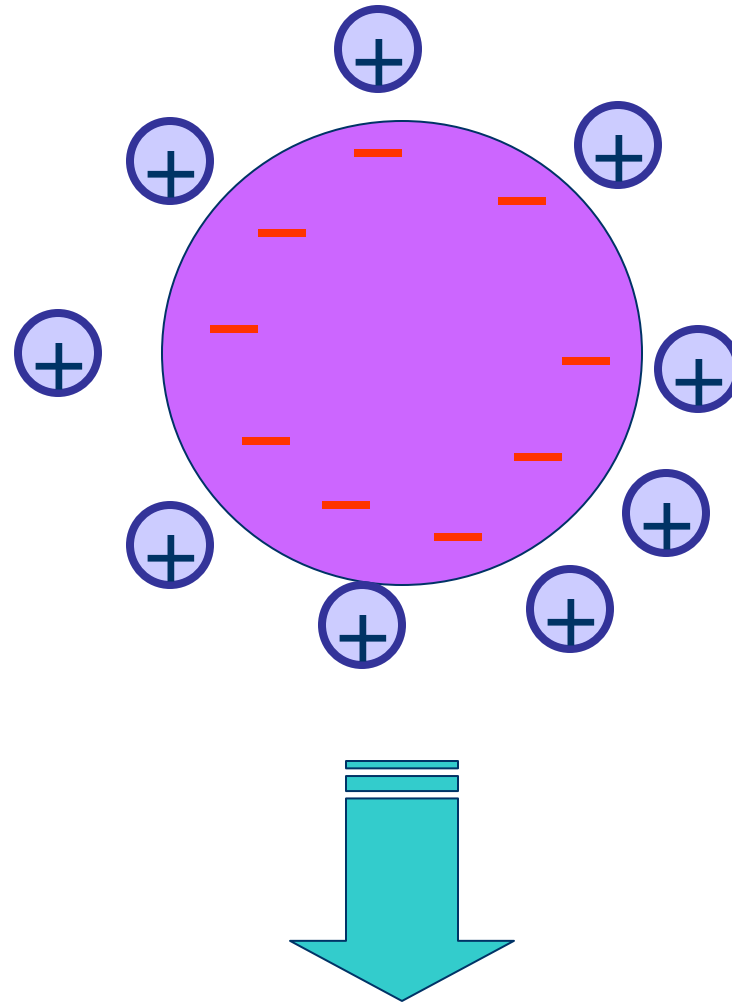


# Kinetic Properties of Colloids

## A. The motion of particles in liquid media

- In this chapter we will consider:
- The thermal motion of colloidal particles.
- The of colloidal particles motion under the influence of gravitational and centrifugal fields.
- However, some aspects of the laws governing the motion of particles through liquids will be consider.

# *Sedimentation of Colloidal Particles*

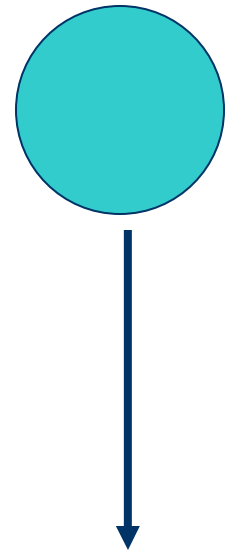


## *Sedimentation rate*

- Consider the sedimentation of an uncharged particle of mass  $m$  and specific volume  $v$  in a liquid of density  $\rho$ .
- The driving (or sedimenting) force, which is independent of particle shape or solvation, is

$$m(1 - v\rho)g,$$

- where  $g$  is the acceleration (gravity or a centrifugal field)



## *Sedimentation rate*

- The liquid medium offers a resistance to the motion of the particle, the resistance of the liquid is, to a first approximation, proportional to the velocity of the sedimenting particle.
- In a very short time, a terminal velocity  $,dx/dt$  ,is attained, when the

Particle driving force = liquid resistance

- The factor  $(1 - v\rho)$  is the buoyancy of the liquid,
- $f$  is the frictional coefficient of the particle in the given medium, which for spherical particles is given by Stokes\* law

$$f = 6\pi\eta a \quad (2.2)$$

## *Sedimentation rate*

where  $\eta$  is the viscosity of the medium, and  $a$  the radius of the particle.

- Therefore, if  $\rho_2$  is the density of a spherical particle (in the dissolved or dispersed state (i.e.  $\rho_2 = 1/v$ ), then

$$(4/3)\pi a^3(\rho_2 - \rho)g = 6\pi\eta a dx/dt$$

*or*

$$dx/dt = 2a^2(\rho_2 - \rho)g / 9\eta$$

# *Sedimentation rate*

- The derivation of Stokes' law assumes that:
- 1. The motion of the spherical particle is extremely slow.
- 2. The liquid medium extends an infinite distance from the particle - i.e. the solution or suspension is extremely dilute.
- 3. The liquid medium is continuous compared with the dimensions of the particle. This assumption is valid for the motion of colloidal particles, but not for that of small molecules or ions which are comparable in size with the molecules constituting the liquid medium.

For spherical colloidal particles undergoing sedimentation, diffusion or electrophoresis, deviations from Stokes' law usually amount to much less than 1 per cent and can be neglected.

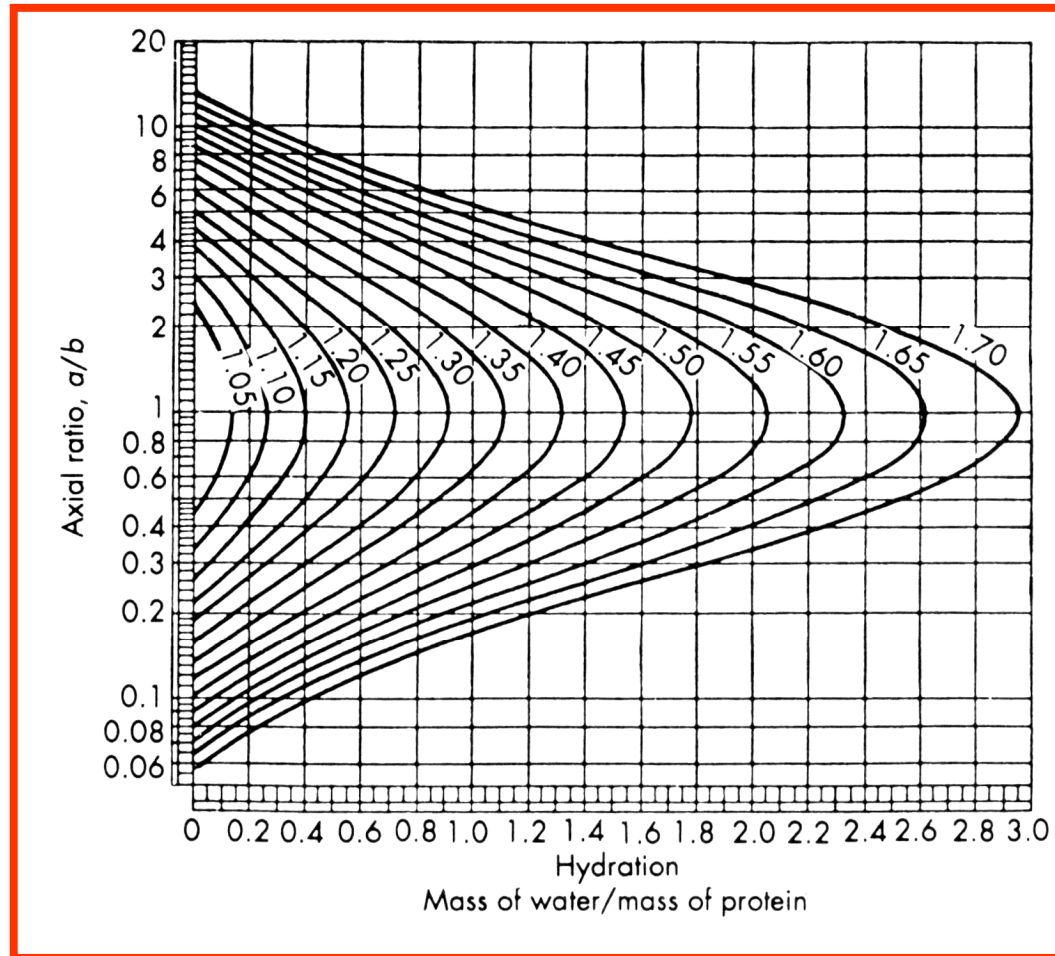
## *Sedimentation rate*

- Fractional ratios The frictional coefficient of an asymmetric particle depends on its orientation. At low velocities such particles are in a state of random orientation through accidental disturbances, and the resistance of the liquid to their motion can be expressed in terms of a frictional coefficient averaged over all possible orientations.
- For particles of equal volume the frictional coefficient increases with increasing asymmetry. This is because, although the resistance of the liquid is reduced when the asymmetric particle is end-on to the direction of flow, it is increased to a greater extent with side-on orientations, so that on average there is an increase in resistance.

## *Sedimentation rate*

- The frictional coefficient is also increased by particle solvation. A particle containing a given volume of dry material will have its smallest possible frictional coefficient,  $f_0$ , in a particular liquid when it is in the form of an unsolvated sphere. The frictional ratio,  $f/f_0$  (i.e. the ratio of the actual frictional coefficient to the frictional coefficient of the equivalent unsolvated sphere) is, therefore, a measure of a combination of asymmetry and solvation.
- If application to dissolved proteins in mind, Oncley 26 has computed frictional ratios for ellipsoids of revolution of varying degrees of asymmetry and hydration. The resulting contour diagram shows the combinations of axial ratio and hydration which are compatible with given frictional ratios. The separate contributions of asymmetry and hydration cannot be determined unless other relevant information is available.

# Sedimentation rate



## B. Brownian motion and translational diffusion

### *Brownian motion*

A fundamental consequence of the kinetic theory is that, in the absence of external forces, all suspended particles, regardless of their size, have the same average translational kinetic energy, which is given by  $(3/2)kT$ , or  $(1/2)kT$  along a given axis-

Then

$$\text{kinetic energy} = \frac{1}{2} m(dx/dt)^2 = \frac{1}{2} kT$$

*i.e. the average particle velocity increases with decreasing particle mass*

## **B. Brownian motion and translational diffusion**

### ***Brownian motion***

- **The motion of individual particles is continually changing direction as a result of random collisions. Each particle pursues a complicated and irregular zig-zag path.**
- **This random motion is referred to as Brownian motion, after the botanist who first observed this phenomenon with pollen grains suspended in water.**

## B. Brownian motion and translational diffusion

### *Brownian motion*

Treating Brownian motion as a three-dimensional “random walk”:

- the mean Brownian displacement,  $\bar{x}$ , of particle from its original position along a given axis after a time  $t$  is given by Einstein's equation:

$$\bar{x} = (2Dt)^{1/2}$$

where  $D$  is the diffusion coefficient.

## B. Brownian motion and translational diffusion

- The diffusion coefficient of a suspended material is related to the frictional coefficient of the particles by Einstein's law of diffusion:

$$Df = kT$$

- Therefore, for spherical particles, where  $f = 6\pi\eta a$

$$D = \frac{kT}{6\pi\eta a} = \frac{RT}{6\pi\eta a N_A}$$

where  $N_A$  is Avogadro's constant, and

$$\bar{x} = (2Dt)^{1/2} = \left( \frac{RTt}{3\pi\eta a N_A} \right)^{1/2}$$

## B. Brownian motion and translational diffusion

$$\bar{x} = (2Dt)^{1/2} = \left( \frac{RTt}{3\pi\eta a N_A} \right)^{1/2}$$

**Perrin (1908) Studied the Brownian displacement and calculated Avogadro's constant varying between  $5.5 \times 10^{23} \text{ mol}^{-1}$  and  $8 \times 10^{23} \text{ mol}^{-1}$ . Subsequent experiment of this nature have yielded values very close to the accepted**

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}.$$

**Note that the correct determination of  $N_A$  constant from observation of Brownian motion provides striking evidence in favor of the kinetic theory.**

## B. Brownian motion and translational diffusion

$$\bar{x} = (2Dt)^{1/2} = \left( \frac{RTt}{3\pi\eta a N_A} \right)^{1/2}$$

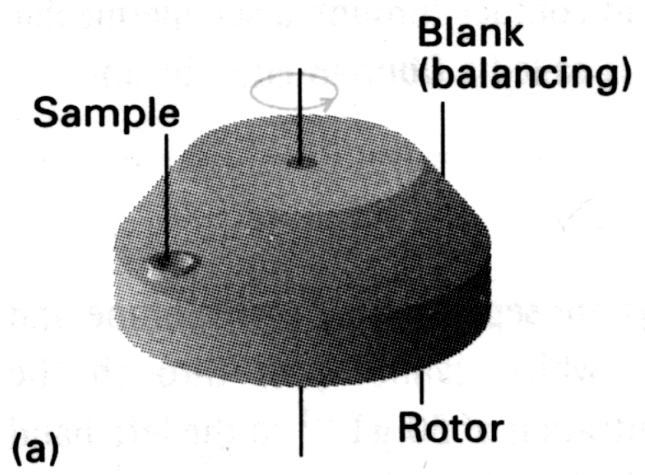
The relation between radius, diffusion coefficients and Brownian displacement

<b>Radius</b>	<b>D/m<sup>2</sup>s<sup>-1</sup></b>	<b><math>\bar{x}</math> after 1h</b>
10 <sup>-9</sup> m (1 nm)	2.1x10 <sup>-10</sup>	1.23x10 <sup>-3</sup> m
10 <sup>-8</sup> m (10 nm)	2.1x10 <sup>-11</sup>	3.90x10 <sup>-4</sup> m
10 <sup>-7</sup> m (100 nm)	2.1x10 <sup>-12</sup>	1.23x10 <sup>-4</sup> m
10 <sup>-6</sup> m (1 $\mu$ m)	2.1x10 <sup>-13</sup>	3.90x10 <sup>-5</sup> m

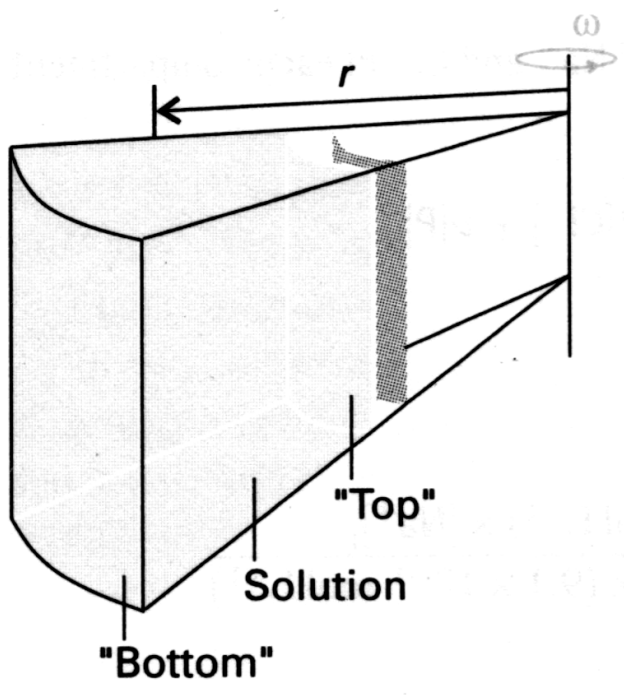
## C. The Ultracentrifuge

- **Sedimentation under gravity** has a practical lower limit 1  $\mu\text{m}$ . Smaller (colloidal) particles sediment so slowly under gravity that the effect is obliterated by the mixing tendencies of diffusion and convection.

Radius	Sedimentation rate
$10^{-9}$ m (1 nm)	$2.2 \times 10^{-12}$ $\text{ms}^{-1}$
$10^{-8}$ m (10 nm)	$2.2 \times 10^{-10}$ $\text{ms}^{-1}$
$10^{-7}$ m (100 nm)	$2.2 \times 10^{-8}$ $\text{ms}^{-1}$
$10^{-6}$ m (1 $\mu\text{m}$ )	$2.2 \times 10^{-6}$ $\text{ms}^{-1}$
$10^{-5}$ m (10 $\mu\text{m}$ )	$2.2 \times 10^{-4}$ $\text{ms}^{-1}$



(a)



(b)



## C. The Ultracentrifuge

- **By employing centrifugal forces** instead of gravity, sedimentation can be extended to the study of colloidal systems, particularly, for the characterization of substances of biological origin, such as proteins, nucleic acids. The driving force, centrifugal forces, becomes

$$m(1 - v\rho)\omega^2 x$$

- Where  $\omega$  is the angular velocity, and
- $x$  the distance of the particle from the axis of rotation

## C. The Ultracentrifuge

- **An ultracentrifuge** is a high-speed centrifuge equipped with a suitable optical system for recording sedimentation behavior and with facilities for eliminating the disturbing effects of convection currents and vibration. The sample is contained in a sector-shaped cell mounted in a rotor (usually ca. 18 cm diameter). Several mechanisms for driving the rotor like an oil turbine. Simpler and less expensive air-driven and electrically driven instruments are now employed.

# The Ultracentrifuge

**The ultracentrifuge can be used in two distinct ways for investigating suspended colloidal material**

- A. The velocity method: a high centrifugal field (up to c. 400 000  $g$ ) is applied and the displacement of the boundary set up by sedimentation of the colloidal molecules or particles is measured from time to time.
- B. The equilibrium method: the colloidal solution is subjected to a much lower centrifugal field, until sedimentation and diffusion (mixing) tendencies balance one another and an equilibrium distribution of particles throughout the sample is attained.

# The Ultracentrifuge

## A. Sedimentation velocity

Equating the driving force on a macromolecule in a centrifugal field with the frictional resistance of the suspending medium,

**And, since**

$$m(1 - v\rho)\omega^2 x = f \frac{dx}{dt}$$

$$Df = kT$$

**but,**

$$\frac{dx}{dt} = \frac{mD(1 - v\rho)\omega^2 x}{kT}$$

$$k = R / N_A$$

$$mN_A = M$$

**then,**

# The Ultracentrifuge

## A. Sedimentation velocity

,  
then,

$$\frac{dx}{dt} = \frac{MD(1 - v\rho)\omega^2 x}{RT}$$

or

$$M = \frac{RTs}{D(1 - v\rho)}$$

$$s = \frac{dx/dt}{\omega^2 x}$$

**Where  $M$  is the molecular mass, and  $s$  is the sedimentation coefficient**

# The Ultracentrifuge

## A. Sedimentation velocity

Given  $s$  as the sedimentation coefficient

$$s = \frac{dx/dt}{\omega^2 x}$$

Integrating

$$s = \frac{\ln x_2/x_1}{\omega^2 (t_2 - t_1)}$$

where  $x_1$  and  $x_2$  are the distance of the boundary from the axis of rotation at times  $t_1$  and  $t_2$ . Therefore,

$$M = \frac{RT \ln x_2/x_1}{D(1 - v\rho)(t_2 - t_1)\omega^2}$$

# The Ultracentrifuge

## A. Sedimentation velocity

### Note that:

- *The system under investigation should remain un-coagulated.*
- *Values for  $s$ ,  $D$  and  $v$  are corrected to a standard temperature, usually 20 °C, and should be extrapolated to zero concentration.*
- *With polydispersed systems either a broadening of the boundary or the formation of distinct peaks representing the various fractions is observed.*
- *Sedimentation does not provide an unequivocal method for establishing the homogeneity of a colloidal system. For example, a mixture of serum albumin and haemoglobin is homogeneous with respect to sedimentation velocity but the two proteins are easily distinguished from each other by electrophoresis.*

# The Ultracentrifuge

## *B. Sedimentation Equilibrium*

- Consider the flow of molecules or particles across an area  $A$  in a colloidal solution where the concentration is  $c$  and the concentration gradient is  $dc/dx$ .

The rate of flow is:

$cA (dx/dt)$  due to sedimentation, and

$-DA (dc/dx)$  due to diffusion (Fick's Law)

*When sedimentation equilibrium is attained, the net flow is zero, so that*

$$c \frac{dx}{dt} = D \frac{dc}{dx}$$

# The Ultracentrifuge

## A. Sedimentation Equilibrium

And, since

$$\frac{dx}{dt} = \frac{MD(1-v\rho)\omega^2 x}{RT}$$

$$\frac{dc}{cdx} = \frac{dx/dt}{D}$$

**then**

$$\frac{dc}{c} = \frac{M(1-v\rho)\omega^2 x dx}{RT}$$

**Integrating**

$$\ln \frac{c_2}{c_1} = \frac{\omega^2 M(1-v\rho)(x_2^2 - x_1^2)}{2RT}$$

**then,**

$$M = \frac{2RT \ln c_2/c_1}{\omega^2 (1-v\rho)(x_2^2 - x_1^2)}$$

# The Ultracentrifuge

## *B. Sedimentation equilibrium*

$$M = \frac{2RT \ln c_2 / c_1}{\omega^2 (1 - v\rho) (x_2^2 - x_1^2)}$$

- *$c_1$  and  $c_2$  are the sedimentation equilibrium concentrations at distances  $x_1$  and  $x_2$  from the axis of rotation. Ideal behaviour has been assumed.*

# The Ultracentrifuge

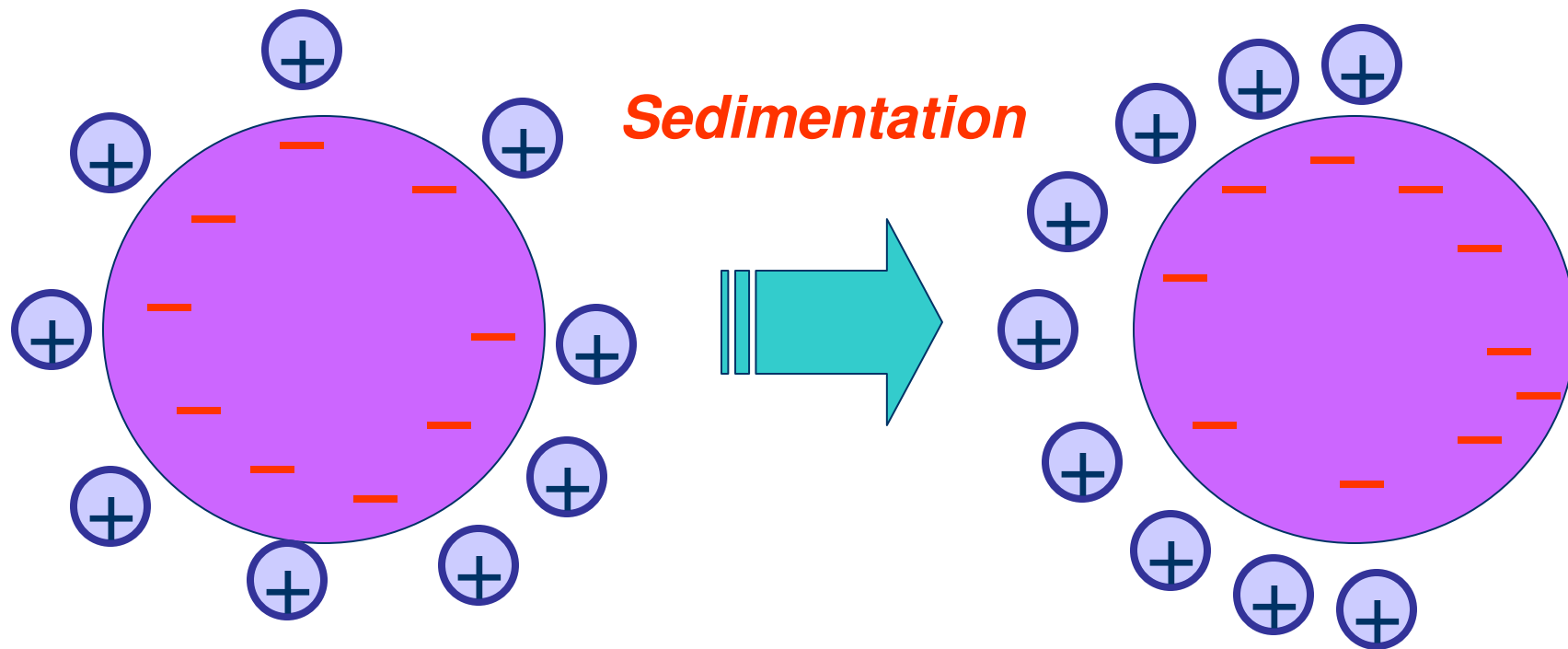
## *B. Sedimentation equilibrium*

- *By sedimentation-diffusion equilibrium, the molecular or particle mass can, therefore, be evaluated without a knowledge of the diffusion coefficient (and, hence, independently of shape and solvation).*
- *Molecular weight obtained by determining relative concentrations at various distances from the axis of rotation. Molecules as small as sugars have been studied by this technique.*
- *Polydispersity introduces complications and is reflected by a drift of  $M$  with  $x$ . Conversely, consistency of  $M$  with  $x$  is an indication of sample homogeneity for  $M$ .*
- *The disadvantage of the sedimentation equilibrium technique is that the establishment of equilibrium may take as long as several days, which is both inconvenient and emphasizes the requirement of avoiding convectional disturbances.*

# The Ultracentrifuge

## *Charge effects*

- *The treatment of sedimentation and diffusion is a little more complicated when the particles under consideration are charged. The smaller counter-ions tend to sediment at a slower rate and lag behind the sedimenting colloidal particles. A potential is thus set up which tends to restore the original condition of overall electrical neutrality by accelerating the motion of the counter-ions and retarding the motion of the colloidal particles.*
- *The reverse situation applies to diffusion. The smaller counter-ions tend to diffuse faster than the colloidal particles and drag the particles along with them and increase their rate of diffusion.*
- *These effects can be overcome by employing swamping electrolyte concentrations. Any potentials which might develop are then readily dissipated by a very small displacement of a large number of counter-ions.*



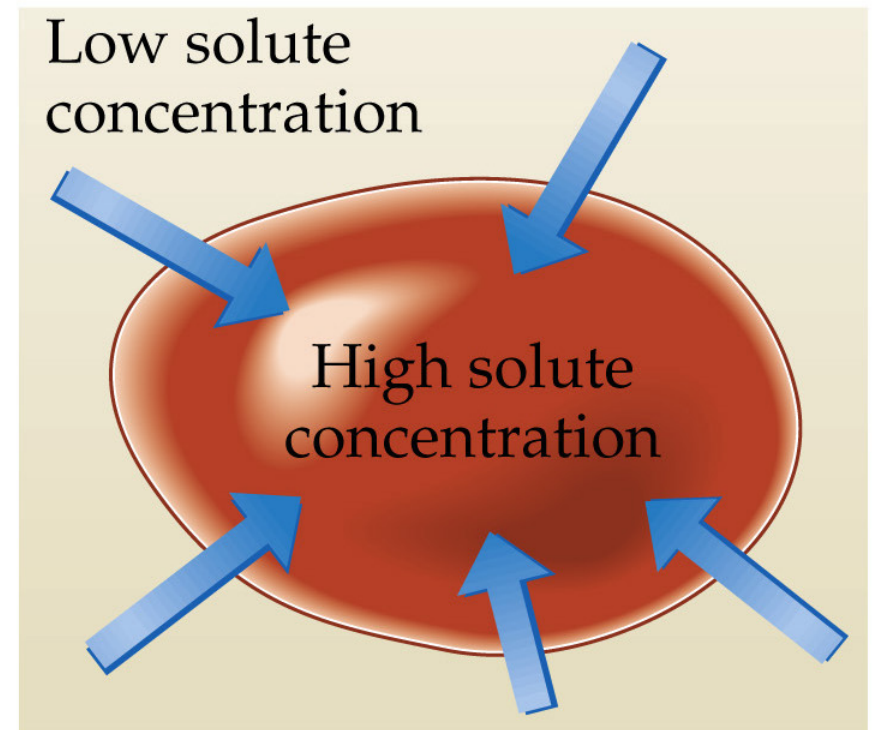
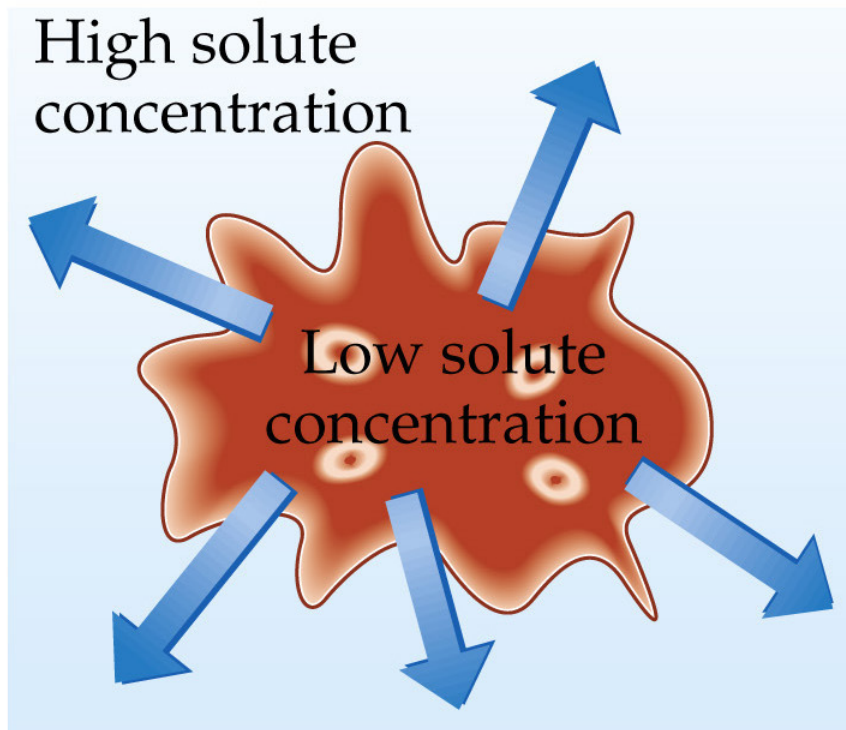
*The smaller counter-ions tend to sediment at a slower rate and lag behind the sedimenting colloidal particles*

# Colligative Properties

- *lowering of vapour pressure,*
  - *depression of freezing point,*
  - *elevation of boiling point and*
  - *osmotic pressure*
- 
- Of these properties, osmotic pressure is the only one with a practical value in the study of macromolecules.

# Colligative Properties

## Osmosis



# Osmosis

## Osmosis

- Hemolysis:
  - red blood cells placed in a hypotonic solution;
  - there is a higher solute concentration in the cell;
  - osmosis occurs and water moves into the cell.
  - The cell bursts.
- To prevent crenation or hemolysis, IV (intravenous) solutions must be isotonic.

# Osmosis

- Cucumber placed in NaCl solution loses water to shrivel up and become a pickle.
- Limp carrot placed in water becomes firm because water enters via osmosis.
- Salty food causes retention of water and swelling of tissues (edema).
- Water moves into plants through osmosis.
- Salt added to meat or sugar to fruit prevents bacterial infection (a bacterium placed on the salt will lose water through osmosis and die).

# Colligative Properties

## Osmosis

- Active transport is the movement of nutrients and waste material through a biological system.
- Active transport is not spontaneous.

**Table 2.3** Molecular data of proteins and other substances in aqueous solution

<i>Name</i>	$\frac{s_{20^\circ\text{C}}}{10^{-13} \text{ s}}$	$\frac{D_{20^\circ\text{C}}}{10^{-11} \text{ m}^2 \text{ s}^{-1}}$	$\frac{v_{20^\circ\text{C}}}{\text{cm}^3 \text{ g}^{-1}}$	$M_r (s)$	$M_r (e)$	$M_r (\pi)$	$f/f_0$	<i>Isoelectric point (pH)*</i>
Urea		129				60		
Sucrose		36				342		
Ribonuclease	1.85	13.6	0.709	12 700	13 000		1.04	
Myoglobin	2.04	11.3	0.741	16 900	17 500	17 000	1.11	7.0
Gliadin	2.1	6.7	0.724	27 500	27 000		1.6	
$\beta$ -Lactoglobulin	3.1	7.3	0.751	41 000	38 000	35 000	1.26	5.2
Ovalbumin	3.55	7.8	0.749	44 000	40 500	45 000	1.16	4.55
Haemoglobin (horse)	4.48	6.3	0.749	68 000	68 000	67 000	1.24	6.9
Serum albumin (horse)	4.46	6.1	0.748	70 000	68 000	73 000	1.27	4.8
Serum globulin (horse)	7.1	4.0	0.745	167 000	150 000	175 000	1.4	
Fibrinogen (bovine)	8.2	2.0	0.706	330 000			2.3	5.2
Myosin	7.2	0.8	0.74	840 000			4.0	5.4
Bushy stunt virus	132	1.15	0.739	10 600 000			1.27	4.1
Tobacco mosaic virus	174	0.3	0.727	59 000 000			2.9	

$M_r (s)$  = relative molecular mass from sedimentation velocity measurements

$M_r (e)$  = relative molecular mass from sedimentation equilibrium measurements

$M_r (\pi)$  = relative molecular mass from osmotic pressure measurements

\*measured at 20°C in acetate or phosphate buffer at an ionic strength of 0.02 mol kg<sup>-1</sup>