Foundations of Colloid Science

Edition 2

Solutions to problems

Chapter 1

**Exercises.** 1.1.1 Give further examples of each of the colloidal systems listed in Table 1.1 and state their approximate composition.

1.1.2 Starting with a cube of solid, 1 cm along each edge, what is the total surface area when the solid is subdivided into cubes $10^{-4}$ cm on each edge? Repeat the calculation for $10^{-5}$ cm and $10^{-6}$ cm cubes. Calculate the surface energy per particle in each case, assuming the surface energy is 70 mJ m$^{-2}$ and compare this to thermal energy ($kT$) at room temperature (25°C). What is the total surface energy for each system?

1.1.3 Show that the surface area per unit mass, $A_m$, of particles of density $\rho$ is given by:

$$A_m = k' \rho r$$

where $r$ is some characteristic dimension, and $k' = 3$ for spheres, 2 for thin cylindrical discs and long rods, and 4 for long square prisms. ($A_m$ is called the specific surface area and typical values for a colloidal material fall in the range $1 - 10^3$ m$^2$ g$^{-1}$).

1.1.4 Chemical bonding energies are commonly of the order 100 kJ. Show that surface energies of particles will approach this value for sizes of about 1 nm. (Assume the surface energy is 0.1 J m$^{-2}$ and take reasonable values for the density and molar mass.)

1.1.5 A mineral oxide of density 2.8 g cm$^{-3}$ is broken up into colloid sized particles in a ball mill. Calculate the total surface area of the crushed material (m$^2$ g$^{-1}$) when the average particle radius is $5 \times 10^{-4}$ cm. What is the total area when the particle radius is 500 Å?

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Solutions 1.1.1 Some interesting ones are:

S/S: light sensitive (or photochromic) glass (a silver halide in glass)

S/L : sump oil - metal particles and carbon in oil.

L/S : wet cement

1.1.2 Total area $= 6 \times 10^4$ cm$^2$ for a $10^{-4}$ cm cube $- 6 \times 10^5$ cm for a $10^{-5}$ cm cube

$= 6 \times 10^6$ cm$^2$ for a $10^{-6}$ cm cube.
Thermal energy = $kT = 3.9 \times 10^{-21}$ J at 298 K.

Surface energy per particle = $4.2 \times 10^{-13}$ J for a $10^{-4}$ cm cube

All much larger than $kT$. Total surface energies for all the particles are 0.42 J, 4.2 J and 42 J respectively.

1.1.3 For a sphere $A_m = 4\pi r^2/[4\pi r^3 + \rho r] - 3/\rho r$.

For a thin disk: $A_m = [2\pi r^2 + 2\pi rh]/[\pi r^2 h] = 2/\rho h$ for $r >> h$

For a long rod, $A_m = 2/\rho r$ for $h >> r$

For a long prism $A_m = [2a^2 + 4ab]/a^2 + 4ab = 4/\rho a$

1.1.4 Assuming $\rho = 2$ g cm$^{-3}$, molar mass = 200, particle size = 1 nm, volume per mole = 100 cm$^3$, total surface energy per mole = $[3\times 100/4\pi r^3] \times 0.1 \times 10^{-4}$ (in Joules for $r$ in cm.) = $(3/r) \times 10^{-3} = 3 \times 10^{-4} = 30$ kJ.

1.1.5 Volume of 1 g = $(1/2.8)$ cm$^3$. Number of particles = $(1/2.8) \times 3/4\pi r^3$. Total area = $3/2.8r = 3/[2.8 \times 5 \times 10^{-4}]$ cm$^2 = 0.21$ m$^2$ g$^{-1}$. At $r = 50$ nm = $5 \times 10^{-6}$ cm, area = $21$ m$^2$ g$^{-1}$.

Exercises

1.4.3 The formation of micelles can be treated as an equilibrium process between monomer molecules (M) and an n-mer:

$nM \leftrightarrow M_n$

How could one determine experimentally whether the entropy change on micellization is positive or negative?

1.4.4 Estimate the radius of the spherical hydrocarbon core of a sodium stearate micelle assuming an aggregation number of 50 and a density for the liquid of 0.9 g cm$^{-3}$. Why do you think a co-surfactant (Fig 1.4.6c) is useful in producing microemulsions?

1.4.5 A kaolinite sample is found to have a surface area of 15 m$^2$ g$^{-1}$. Assuming that the particles are cylindrical discs of density 2.8 g cm$^{-3}$ and aspect ratio 1:10, estimate the average radius. (This is called the area average size. (section 5.3)). How many double (Al/Si) sheets are involved in this average crystal?

1.4.6 Israelachvili and Adams (1978) in their direct measurements of the forces between two mica sheets quote the following composition (by mass) for one of their micas:

$\Sigma 1.2$

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\[ \text{SiO}_2 \quad \text{Al}_2\text{O}_3 \quad \text{FeO} \quad \text{MgO} \quad \text{Na}_2\text{O} \quad \text{K}_2\text{O} \quad \text{H}_2\text{O} \text{ (assumed)} \]
\[45.94 \quad 37.29 \quad 0.96 \quad 0.56 \quad 0.93 \quad 10.14 \quad 4.19\]

Compare this with the theoretical structure and suggest a likely arrangement. (Assume that
divalent ions can substitute for Al\(^{3+}\) and that Al\(^{3+}\) can substitute for silicon to create sufficient
charge to neutralize the Na\(^+\) and K\(^+\).) [Hint: convert the composition to a molar basis first.]

1.4.7 The thickness of montmorillonite platelets is 0.97 nm. Calculate the maximum
expected surface area of a montmorillonite sample assuming its density is 2.8 g cm\(^{-3}\). If this
material has a cation exchange capacity (c.e.c.) of 1 mol kg\(^{-1}\) of monovalent ions, how far apart,
on average, are the exchangeable cations? Repeat the calculation for the kaolinite sample in
Exercise 1.4.5 assuming the c.e.c is 50 mmol kg\(^{-1}\) and the ions are confined to the basal planes.

1.4.8 What is the relationship between the charges per unit cell in white mica,
vermiculite and montmorillonite?

---

1.4.3 \( K = [M_n]/[M]^n \) and \( \Delta G_{m,0} = -RT \ln K \). But \( dG = VdP - SdT \) so \( \Delta S_m = -[\partial \Delta G_{m,0}/\partial T]_p \).

If one assumes that all the soap (above the cmc) is in the form of micelles, and that there
is plenty of soap (total concentration \( C \)) then

\[ [M] \sim \text{c.m.c} \sim c \quad \text{and} \quad [M_n] \sim (\text{conc of soap} - \text{c.m.c.})/n \sim (C - c)/n \sim C/n. \]

\[ K \sim C/n c^n \quad \text{and} \quad \ln K = \ln C - \ln n - n \ln c. \]

\[ \Delta S_m^0 = \left[ \ln K + \left( \frac{\partial \ln K}{\partial \ln T} \right) \right] \quad \text{and} \quad \frac{\partial \ln K}{\partial \ln T} = -n \frac{\partial \ln c}{\partial \ln T} \]

\[ \therefore \Delta S_m^0 = \left[ \ln K - n \left( \frac{\partial \ln c}{\partial \ln T} \right) \right] \]

Knowing the equilibrium constant at some reference temperature and how the cmc varies with
temperature should allow one to determine the entropy change on micellisation provided that
the degree of association does not change much with temperature.

1.4.4 Stearate has 17 carbons in the hydrocarbon core. With an aggregation number of 50, this
is a total of 850 CH\(_3\)s. The mass of such a micelle would be 850\times 14 amu corresponding to a
volume of \( 850\times 14/0.9\times 6.023\times 10^{23} \) cm\(^3\) and a radius of \( 1.74\times 10^{-7} \) cm = 1.74 nm. Adding a co-
surfactant increases the attractive interactions between the chains whilst reducing the head group

\[ S 1.3 \]

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repulsion.

1.4.5 Area of disc = 2πa² + 2πab with a = 5b so Area = 2.4 πa² and Volume = 0.2 πa³.
Number of particles in 1 g = N and these have total volume of 1/2.8 cm³. Hence
N = 1/(2.8 × 0.2πa³) . Area = N × 2.4πa² = 4.286/a = 15 × 10⁴ cm².
Hence a = 0.29 × 10⁻⁴ cm = 0.29 μm. Number of Al/Si pairs = 0.29 μm/0.71nm = 400.

1.4.6 Molar composition is:

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.729</td>
<td>0.366</td>
<td>0.014</td>
<td>0.014</td>
<td>0.015</td>
<td>0.108</td>
<td>0.233</td>
</tr>
</tbody>
</table>

We require 0.246 - 0.028 = 0.218 mol of Al³⁺ to substitute for Si, assuming that the
divalent ions (Fe²⁺ and Mg²⁺) all substitute for Al in the octahedral layer. There are 2 × 0.366
= 0.732 mole of Al³⁺ altogether, so this leaves 0.514 moles of Al³⁺ in the octahedral layer and
the SiO₂ layer will have about 0.218 × 100/(0.729 + 0.218) = 23% substitution - almost exactly the
25% required for the ideal crystal.

1.4.7 Assume the platelets all separate and the edge area can be ignored. The platelets can be
arranged in a stack of area 1 cm² and height (1/2.8) cm to give a volume of 1/2.8 cm³. There
will be (1/2.8) / 0.97 × 10⁻⁷ layers in the stack. The area is therefore 2/(2.8 × 0.97 × 10⁻⁷) =
7.36 × 10⁶ cm² = 736 m²/g. Area per exchangeable ion is then 736 × 10⁻⁶ × 10⁻²³ m² = 1.23 × 10⁻¹⁸ m²
so the average spacing is 1.1 × 10⁻⁹ m = 1.1 nm.

For kaolinite the area per ion is (15 × 10⁶ cm²) / (50 × 10⁻⁶ × 6 × 10³) = 5 × 10⁵ cm⁻². The
separation is then 7 × 10⁻⁹ cm = 0.7 nm. The charge density is actually higher in this case.

1.4.8 Ratio is 3:2:1. (0.25:0.16:0.083). Note that there is twice as much SiO₂ as Al₂O₃ in each
cell.

Exercises. 1.5.1 (i) Establish eqn (1.5.4) from (1.5.2) and (1.5.3).
(ii) Establish eqn (1.5.5) from (1.5.4).

1.5.2 Use the identity

S 1.4
\[
\Gamma(\frac{1}{2}) = \int_{0}^{\infty} \exp(-p)p^{-\frac{1}{2}}dp = \pi^{\frac{1}{2}}
\]

to evaluate \( k' \) in eqn (1.5.7).

1.5.3 Use the more exact form of Stirling's approximation:
\[
\ln N! = (N+\frac{1}{2})\ln N - N + \ln(2\pi)^{\frac{1}{2}}
\]
to show that
\[
P = \left( \frac{2}{\pi m} \right)^{\frac{1}{2}} \exp \left( -\frac{x^2}{2m^2} \right)
\]
(Note the disappearance of \( l \) from the pre-exponential factor because this form applies to the discrete distribution, confining the particle to points distant \( l \) apart.) Why does it also contain a factor two compared to 1.5.8?

1.5.4 Verify by direct differentiation that eqn (1.5.21) is a solution of eqn (1.5.20) and, hence, establish (1.5.22).

1.5.5 Use the identity:
\[
\int_{0}^{\infty} x^2 \exp(-ax^2)dx = \frac{1}{4a} (\pi a)^{\frac{3}{2}}
\]
to show that \( <x^2>^{\frac{1}{2}} \) is equal to \( \sigma \).

1.5.1 (i)

\[
P = \frac{m!}{[\frac{1}{2}(m+s)]![\frac{1}{2}(m-s)]!2^{m}}
\]

\[
\ln P = \ln(m!) - \ln(\frac{1}{2}(m+s))] - \ln(\frac{1}{2}(m-s)] - m \ln 2
\]
\[
= \ln m - m - \frac{1}{2}(m+s)\ln[\frac{1}{2}(m+s)] + \frac{1}{2}(m+s) - \frac{1}{2}(m-s)\ln[\frac{1}{2}(m-s)] + \frac{1}{2}(m-s) - m \ln 2
\]
\[
= \ln m - m \ln 2 - \frac{1}{2}(m+s)\ln[1/s] - \frac{1}{2}(m+s)\ln(1-s/m) - \frac{1}{2}(m-s)\ln[1] - \frac{1}{2}(m-s)\ln(m) - \frac{1}{2}(m-s)\ln m
\]
\[
\ln P = m \ln m - \frac{1}{2}(m+s)\ln(1+s/m) - \frac{1}{2}(m-s)\ln(1-s/m) - m \ln m \quad \text{from which equation 1.5.4 follows}
\]

\[ \mathbb{S} \{ 1.5 \} \]

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immediately.

(ii)

\[
-\ln P = \frac{1}{2}(m+s)\left[\frac{s}{m} - \frac{s^2}{2m^2}\right] + \frac{1}{2}(m-s)\left[\frac{s}{m} - \frac{s^2}{2m^2}\right]
\]

\[
= \frac{s^2}{2m} + \frac{s^2}{2m} - \frac{s^2}{4m} - \frac{s^2}{4m} - \frac{s^3}{4m^2} - \frac{s^3}{4m^2} = \frac{s^2}{2m}
\]

Then \( \ln P = -\frac{s^2}{2m} = -\frac{x^2}{2ml^2} \).

1.5.2

\[
\Gamma(\frac{1}{2}) = \int_0^\infty \exp(-p) p^{-\frac{1}{2}} dp = \sqrt{\pi}
\]

\[
k' = 2\int_0^\infty \exp\left(\frac{-x^2}{2ml^2}\right) dx
\]

Put \( p = \frac{x^2}{2ml^2} \) so that \( x = (2ml^2)p^{\frac{1}{2}} \) and \( dx = \frac{1}{2}(2ml^2)^{\frac{3}{2}} p^{-\frac{1}{2}} dp \)

\[
k' = \left[2\int_0^\infty \exp(-p) p^{-\frac{1}{2}}(2ml^2)^{\frac{3}{2}} dp\right]^{\frac{1}{2}} = [(2ml^2\pi)^{\frac{3}{4}}]^{\frac{1}{2}}
\]

so \( k' = (2\pi ml^2)^{\frac{3}{4}} \).

1.5.3 From exercise 1.5.1, using the better approximation for the factorial:

\[
\ln P = -\frac{m+s}{2}\ln(1+s/m) - \frac{m-s}{2}\ln(1-s/m) + \frac{1}{2}\ln m + \ln(2\pi)^{x/6}
\]

\[-\frac{1}{2}\ln\frac{m+s}{2} - \ln(2\pi)^{\frac{3}{2}} - \frac{1}{2}\ln\frac{m-s}{2} - \ln(2\pi)^{\frac{3}{2}}
\]

\[= \frac{m+s}{2}\ln(1+s/m) + \frac{m-s}{2}\ln(1-s/m) + \ln\frac{\pi}{2m} + \frac{1}{2}\ln(m^2 - s^2)
\]

\[
S \sqrt{c}
\]

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But \( s/m < 1 \) so \( m^2 - s^2 = m^2 \) and \( s^2 = x^2/l^2 \). Also using the result of exercise 1.5.1 (ii):

\[
-\ln P = \frac{x^2}{2ml^2} + \ln\left[\frac{\pi}{2m}\right]^{\frac{1}{2}} + \ln m = \frac{x^2}{2ml^2} + \ln\left[\frac{\pi m}{2}\right]^{\frac{1}{2}}
\]

So

\[
P = \left[\frac{2}{\pi ml}\right]^{\frac{1}{2}} e^{-\frac{x^2}{2ml^2}}
\]

1.5.4

\[
c(x,t) = c_0 \left[\frac{\tau}{2\pi l^2 t}\right]^{\frac{1}{2}} e^{-\frac{\tau x^2}{2l^2 t}}
\]

\[
\frac{\partial c}{\partial t} = -\frac{\partial c_0}{\partial t}\left[\frac{\tau}{2\pi l^2 t}\right]^{\frac{1}{2}} e^{-\frac{\tau x^2}{2l^2 t}} + c_0 \left[\frac{\tau}{2\pi l^2 t}\right]^{\frac{1}{2}} e^{-\frac{\tau x^2}{2l^2 t}} \frac{\tau x^2}{2l^2 t} \frac{1}{t^2}
\]

\[
= c(x,t) \left[\frac{1}{2l} + \frac{\tau x^2}{2l^2 t} \frac{1}{t^2}\right] = c(x,t) \left[\frac{x^2}{2l t} - 1\right]
\]

\[
\frac{\partial c}{\partial x} = c_0 \left[\frac{\tau}{2\pi l^2 t}\right]^{\frac{1}{2}} e^{-\frac{\tau x^2}{2l^2 t}} \frac{\tau x}{l^2 t}
\]

\[
D \frac{\partial^2 c}{\partial x^2} = \left[\frac{-\tau x}{l^2 t} \frac{\partial c}{\partial x} - \frac{c(x,t)\tau}{l^2 t}\right] D
\]

\[
= \left[\frac{x^2}{l^2 t} c(x,t) - \frac{c(x,t)\tau}{l^2 t}\right] D
\]

\[
= \frac{c(x,t)}{2t} \left[\frac{x^2}{l^2 t} - 1\right] 2D \frac{\tau}{l^2}
\]

Obviously, \( \partial c/\partial t = D\partial^2 c/\partial x^2 \) if \( 2D\tau l^2 = 1 \)

§ 1.7

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\[
<\chi^2>_{\infty} = \left[ \frac{1}{\sigma_0 \sigma_\infty} \int_{-\infty}^{\infty} x^2 c(x,\tau) \, dx \right]_{\infty}^{\infty} = \left[ \frac{2}{\sigma_0 \sigma_\infty} \int_{0}^{\infty} x^2 c(x,\tau) \, dx \right]_{\infty}^{\infty}
\]

But \( c(x,\tau) = \sigma_0 \left( \frac{\tau}{2 \pi \tau^2} \right)^{\frac{1}{2}} \exp \left( -\frac{\pi x^2}{4 \tau} \right) \) and \( \tau = \frac{t^2}{2D} \)

\[
= \sigma_0 \left( \frac{1}{4 \pi D \tau} \right)^{\frac{1}{2}} \exp \left( -\frac{x^2}{4 D \tau} \right).
\]

Therefore

\[
<\chi^2>_{\infty} = \left[ \frac{1}{(4 \pi D \tau)^{\frac{1}{2}}} \int_{0}^{\infty} x^2 \exp \left( -\frac{x^2}{4 D \tau} \right) \, dx \right]_{\infty}^{\infty}
\]

\[
= \left[ \frac{2}{(4 \pi D \tau)^{\frac{1}{2}}} D \sqrt{\pi} \right]^{\frac{1}{2}} = \sqrt{2D \tau}
\]

\[
= \sqrt{\frac{t^2}{\tau}} = (t^2 m)^{\frac{1}{2}} = m^{\frac{1}{2}} \tau = \sigma
\]
Solutions
Chapter 2

Exercises. 2.2.1 Calculate the number of molecules in 1 cm$^3$ of water from the molar volume (18 cm$^3$). If it is in the shape of a 1 cm cube show that the ratio of surface energy to bulk energy is approximately $10^{-7}$. How big a collection of molecules would be needed so that the surface energy was the same as the bulk energy?

2.2.2 Consider the increase $dA$ in area of a small surface element and the concomitant volume, $dV$ traversed by the surface (Fig. 2.2.6). Show that $dA = (1/R_1 + 1/R_2)dV$ where $R_1$ and $R_2$ are as defined in section 2.2.3 above.

2.2.3. Use the result derived in Exercise 2.2.2 to establish the Young-Laplace equation using an energy minimization argument.

2.2.4. Calculate the excess pressure inside drops of water of radius $10^{-5}$ cm and $10^{-6}$ cm, respectively. (Take $\gamma = 70$ mN m$^{-1}$.)

Solutions 2.2.1 No of molecules in 1 cm$^3 = 6.023 \times 10^{23}/18 = 3.35 \times 10^{22}$. No of molecules along each side edge of cube = $(3.35 \times 10^{22})^{1/3} = 3.222 \times 10^{7}$. No of molecules in surface = $6 \times 3.222 \times 10^{7} = 6.23 \times 10^{15}$. Surface/bulk energy = $(\varepsilon_{AA}\sigma_{AA}^2) \times \text{(no of surface molecules/no of bulk molecules)} = \frac{1}{2} \times 6.23 \times 10^{15}/3.35 \times 10^{22} = 10^{-7}$.

2.2.2 Area $A = R_1 \delta \theta_1 R_2 \delta \theta_2$; Area $A + dA = (R_1 + dR) \delta \theta_1 (R_2 + dR) \delta \theta_2$.

So $dA = R_1 \delta \theta_1 \delta \theta_2 \ dR + dR \delta \theta_1 \delta \theta_2 R_2 + \text{terms of order } (dR)^2$.

$dV = AdR = R_1 R_2 \delta \theta_1 \delta \theta_2 dR$.

Hence $dA/dV = (R_1 + R_2) dR/R_1 R_2 = (1/R_1 + 1/R_2) dR$.

2.2.3 The work done in expanding the surface by $dR$ is equal to the net force acting across it: $(p' - p) dA$ multiplied but the distance through which it moves.

So the work done is $(p' - p) dA dR = (p' - p) \gamma dV$.

If the energy involved is to be minimised then this work, plus the surface work, must sum to zero: $(p' - p) dV + \gamma dA = 0$ and so:

S2.1
\[(p^*-p^')dV = -\left[\frac{1}{R_1} + \frac{1}{R_2}\right] \gamma dV\]

from which the Young-Laplace equation follows immediately.

2.2.4  (i) \(p^* - p' = 2 \times 70 \times 10^{3}/10^{-7} = 1.4 \times 10^6 \text{ N m}^{-2} = 14 \text{ atm.}\)

(ii) \(p^* - p' = 1.4 \times 10^7 \text{ N m}^{-2} = 140 \text{ atm.}\)

---

Exercises 2.3.1 Establish eqns (2.3.27), (2.3.28), and (2.3.30).

2.3.2 The surface excess Gibbs free energy may be defined either as

\[ G = U^0 - TS^0 + pV^0 \]

or

\[ G = U^0 - TS^0 + pV^0 - \gamma A. \]

Show that the latter definition leads to

\[ G^0 = \sum \mu_i \rho_i^0 \]

which is analogous to the bulk phase equation (eqn (A5.26)). [Note that \(V^0 = 0\) in the Gibbs model.]

---

Solutions 2.3.1 \(F = U - TS - U^* - TS^* + U^* - TS^* + U^0 - TS^0\)

So \(F^0 = U^0 - TS^0 = \gamma A + \sum \mu_i \rho_i^0\)  \(\text{ (from eqn 2.3.27)}\)

Then \(dF^0 = dU^0 - TdS^0 - S^0 dT\). But from (2.3.14) \(dU^0 = -TdS^0 + \gamma dA + \sum \mu_i d\rho_i^0\)

(since the \(\mu_i\)s are constant) and so: \(dF^0 = -S^0 dT + \gamma dA + \sum \mu_i d\rho_i^0\).

2.3.2 \(G^0 - U^0 - TS^0 + pV^0 - \gamma A = U^0 - TS^0 - \gamma A\) in the Gibbs model \(V^0 = 0\) = \(\sum \mu_i \rho_i\) (from (2.3.25)).

---

Exercises 2.4.1 Imagine a sharply defined surface layer of adsorbed material at the liquid-vapour interface. By placing the Gibbs dividing surface at the boundary between the adsorbed layer and the liquid, use eqn (2.4.8) to show that the relative adsorption \(\Gamma_{i,1}\) is zero when \(\Gamma_{i}/x_i = \Gamma_{i}/x_i'\)

i.e. when the components \(i\) and \(1\) are present in the same molar ratio in the surface layer as they
are in the liquid. Show also that $\Gamma_{ij}$ is positive if the surface layer is relatively richer in $i$, negative if the surface layer is relatively poorer in $i$.

2.4.2 Establish eqn (2.4.18).

2.4.3 Establish eqn (2.4.7) and (2.4.11).

2.4.4 If two phases, ('') and (""') are in contact at constant $T$ and $p$, the Gibbs-Duhem equation requires that $\sum \gamma_i d\mu_i = 0$ in each phase. Consider the situation where solute 3 is distributed between the bulk solvents 1 and 2. Show that the surface excess of solute 3 relative to 1 and 2 is given by:

$$\Gamma_{3,12} = \Gamma_3 - \frac{\Gamma_3(n_3''n_2' - n_3'n_2') - \Gamma_2(n_1'n_3' - n_1'n_3)}{n_2'n_1' - n_2'n_1}$$

(Hint: refer back to eqn (2.4.3) and use the Gibbs-Duhem equations to eliminate $d\mu_1$ and $d\mu_2$. Note the similarity to eqn (2.4.30).)

2.4.5 Show that if the two solvents 1 and 2 in Exercise 2.4.4 are mutually insoluble then

$$\Gamma_{3,12} = \Gamma_3 - \frac{n_3'}{n_1'}\Gamma_1 - \frac{n_3''}{n_2''}\Gamma_2$$

2.4.6 Consider the system indicated below where the data for the surface region is obtained from a sample which contains some bulk phase:

<table>
<thead>
<tr>
<th></th>
<th>Oil</th>
<th>Water</th>
<th>Solute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk oil</td>
<td>0.96</td>
<td>0.09</td>
<td>0.24</td>
</tr>
<tr>
<td>Surface region</td>
<td>0.84</td>
<td>1.02</td>
<td>0.51</td>
</tr>
<tr>
<td>Bulk water</td>
<td>0.36</td>
<td>1.08</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Calculate the surface excess of solute in this case, relative to both oil and water, using the relation in exercise 2.4.4. (Assume the area of the interface from which the sample is taken is 250 cm$^2$.)

2.4.7 What is the surface version of the Gibbs-Duhem relationship (cf. eqn. A5.23)?

2.4.8 Repeat the calculation in exercise 2.4.6 using the Guggenheim (1976) concept of a surface phase which has a finite thickness and is defined by boundaries placed inside both the bulk phases. To solve the problem, ensure first that you place the boundaries in each phase so that the surface excess of both water and oil is zero. Hence calculate the surface excess of

S2.3
the solute and verify that the result is the same as in exercise 2.4.6.

Solutions 2.4.1 This follows directly from (2.4.12) which applies in this case. Obviously, if the r.h.s. of eqn (12) is written \( x'_i [\Gamma'_i/x'_i - \Gamma'_j x'_j] \) it is evident that if \( \Gamma'_i/x'_i > \Gamma'_j/x'_j \) then \( \Gamma_{i,j} \) is positive and vice versa since \( x'_i > 0 \).

2.4.2

\[
\Gamma_{i,j} = -\frac{1}{R \tau} \frac{d\gamma}{d\ln a_2} = -\frac{1}{R \tau} a_2 \frac{d\gamma}{d a_2} = -\frac{x_2 y_2}{R \tau} \left[ 1 + \frac{x_2}{y_2} \frac{d\gamma}{d x_2} \right]^{-1}
\]

from which eqn (2.4.18) follows immediately.

2.4.3 The Gibbs Adsorption Isotherm is:

\[
d\gamma = \Gamma_1 d\mu_1 + \sum_{i=2}^{N} \Gamma_i d\mu_i \tag{2.4.6}
\]

and substituting from eqn (2.4.6) for \( d\mu_i \):

\[
d\gamma = \left[ -\sum_{i=2}^{N} \frac{(c_i - c_i^{\infty})}{(c_i^{\infty} - c_i)} d\mu_i \right] \Gamma_1 + \sum_{i=2}^{N} \Gamma_i d\mu_i
\]

from which eqn (2.4.7) follows immediately.

From (2.4.10) \( V^{\infty} = n_1^0 \Delta c_1 - (n_1 - Vc_1) \Delta c_1 \) and so from eqn (2.4.9):

\[
n_i^0 = (n_i - Vc_i) + \left[ \frac{n_i \Delta c_i}{\Delta c_1} - (n_i - Vc_1) \frac{\Delta c_i}{\Delta c_1} \right]
\]

which rearranges to eqn (2.4.11).

2.4.4 \( d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \Gamma_3 d\mu_3 \) \( (1) \) But \( n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 = 0 \) \( (2) \)
and \( n_1 \, d\mu_1 + n_2 \, d\mu_2 + n_3 \, d\mu_3 = 0 \) (3) from the Gibbs - Duhem equation (A.5.23).

Then multiplying (2) by \( n_1 \) and (3) by \( n_1 \) and subtracting gives:

\[
(n_2 \, n_1 - n_2 \, n_1 \, d\mu_2 + (n_3 \, n_1 - n_3 \, n_1 \, d\mu_3 = 0 \quad \text{and so:}
\]

\[
\frac{n_1 \, n''_3 - n_1 \, n'_3}{n_1 \, n'_2 - n_2 \, n_1} d\mu_1 = \frac{n_1 \, n''_3 - n_1 \, n'_3}{n_1 \, n'_2 - n_2 \, n_1} d\mu_3
\]

Likewise:

\[
d\mu_3 = \frac{n_2 \, n''_3 - n_2 \, n'_3}{n_2 \, n'_2 - n_2 \, n_1} d\mu_2
\]

Substituting this in equation (1) gives:

\[
- \, dY = \left\{ \Gamma_3 - \Gamma_3 \frac{n_2 \, n'_3 - n_2 \, n''_3}{n_2 \, n'_2 - n_2 \, n_1} + \Gamma_3 \frac{n_1 \, n''_3 - n_1 \, n'_3}{n_1 \, n'_2 - n_2 \, n_1} \right\} d\mu_3
\]

The expression in the braces is \( \Gamma_{3,12} \).

2.4.5 If the solvents are mutually insoluble then \( n_1'' = n_2'' = 0 \) and so

\[
\Gamma_{3,12} = \Gamma_3 - \Gamma_3 \frac{n_2' - n_2''}{n_1' - n_2''} + \Gamma_3 \frac{0 - n_1'n_2''}{n_1' - n_2''} = \Gamma_3 - \frac{n_1 T_2}{n_1'} - \frac{n_2 T_2}{n_2''}
\]

2.4.6 Component 1 2 3 Phase

Water Oil Solute

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th>-b</th>
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<tbody>
<tr>
<td>1.08</td>
<td>0.36</td>
<td>0.18</td>
<td>Xle</td>
<td>β or '</td>
</tr>
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</table>

<p>| | | | | |</p>
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<tbody>
<tr>
<td>0.09</td>
<td>0.96</td>
<td>0.24</td>
<td>Xle</td>
<td>α or &quot;</td>
</tr>
</tbody>
</table>

Using the values in the table the calculation, from the results in Exercise 2.4.5 is

S2.5

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\[ \Gamma_{\alpha,12} = 0.51 - [1.02(0.96 \times 0.18 - 0.36 \times 0.24) - 0.84(0.09 \times 0.18 - 1.08 \times 0.24)]/(0.96 \times 1.08 - 0.36 \times 0.09) = 0.51 - 0.292/1.004 = 0.219 \text{ \mu mole in } 250 \text{ cm}^2 - 8.76 \times 10^{-10} \text{ mole cm}^2. \]

2.4.7 The Gibbs Adsorption Equation (2.4.2).

2.4.8 We have to expand the interfacial region in such a way as to simultaneously make the excess of water and of oil, zero. We need an extra 0.15 moles of water, some of which comes from the upper (β) phase and some from the lower (α) phase. To find out how much comes from each we must ensure that we also get the correct extra number of moles of oil (i.e. 0.96 + 0.36 - 0.84 = 0.48). Thus if \(a\) moles of water came from the bulk phase \(α\) and (0.15 - \(a\)) from phase \(β\) they will be accompanied by \((0.96 + a)/0.09 + 0.36(0.15 - a)/1.08\) extra moles of component 2 (the oil). Setting this equal to 0.48 gives \(a = 0.0416\). This 0.0416 moles of component 1 will be accompanied by an extra 0.0416 \times 0.24/0.09 = 0.1109 \text{ \mu moles of component 3}. Likewise, the (0.15 - 0.0416) = 0.1084 moles which come from phase \(β\) will carry an extra 0.1084 \times 0.18/1.08 = 0.0181 \text{ \mu moles of component 3}. Surface excess of 3 is therefore: \([0.51 + 0.1109 + 0.0181 - 0.24 - 0.18] \times 10^{-6}/A_s = 8.76 \times 10^{-10} \text{ moles cm}^2\) as before.

Exercises. 2.5.1 Estimate the value of \(p^*/p\) for a droplet of water and \(p^*/p\) for a bubble in water with the following radii: \(r = 10^{-8}\text{ m}, 10^{-7}, 10^{-6}, 10^{-5}\text{ m}.\) (Note that the last result is unlikely to be correct. Why?) Take \(T = 18^\circ\text{C}\), \(\rho_l = 18 \text{ cm}^3\text{ mol}^{-1};\) \(\gamma = 73 \text{ mN m}^{-1}.\) Calculate values for \(p^* - p^*\) across an interface with these radii. How do these figures relate to the boiling process for water?

2.5.2 Derive eqns (2.5.12) and (2.5.14) and show that they yield the approximate expressions under the conditions stated. How much effect does the approximation have on the calculated values for \(r = 5 \times 10^{-9}\text{ m}\)?

2.5.3 Show that if \(\Delta_R_{ucp} = a - bT\) where \(a\) and \(b\) are constants, the integration in section 2.5.3(b) leads to:

\[ a\left(\frac{1}{T_0} - \frac{1}{T}\right) - b\ln\frac{T}{T_0} = R\ln(1 + 2\gamma/rp^*). \]

S2.6
The form for $\Delta H^\circ_{\text{cap}}$ is suggested by Kirchhoff's law with a constant value of

$$
\Delta C^p = C^p_{\text{cap}} - C^p_{\text{ps}}.
$$

This is a more precise form of eqn (2.5.18).


2.5.4 Check the values given in Table 2.3 by back-calculating the value of $r$ from the given values of $T$, $\gamma$, and $\Delta H^\circ_{\text{cap}}$, using the more exact formula derived in Exercise 2.5.3.

**Solutions**

2.5.1 From eqn (2.5.12) for a droplet: $\ln p \gamma p^0 = 2\gamma V^\prime rRT$ for $V^\prime << V^\prime$. (Note that $p^\prime$ is the pressure in the vapour phase.) $(V^\prime)$ is the molar volume here (the overline on $V$ doesn't work too well in this text.)

$$
\ln p \gamma p^0 = \left[2 \times 73 \times 10^{-3} \times 18 \times 10^{-6}\right](10^{-6} \times 8.314 \times 291) \quad \text{for} \quad r = 10^{-6} \text{ m.} \quad \text{So} \quad p \gamma p^0 = 1.001.
$$

Other values are given in Table 2.2.

<table>
<thead>
<tr>
<th>$r$/m</th>
<th>$10^{-6}$</th>
<th>$10^{-7}$</th>
<th>$10^{-8}$</th>
<th>$10^{-9}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln p \gamma p^0$</td>
<td>-0.0011</td>
<td>-0.01086</td>
<td>-0.1086</td>
<td>-1.087</td>
</tr>
<tr>
<td>$p \gamma p^0$</td>
<td>0.9989</td>
<td>0.989</td>
<td>0.897</td>
<td>0.337</td>
</tr>
</tbody>
</table>

$r$/m

$$
\ln p \gamma p^0 = -2\gamma V^\prime rRT
$$

$\ln p \gamma p^0 = 1.46 \quad 14.6 \quad 146 \quad 1460 \times 10^5 \text{ N m}^{-2}$

(Note: $10^5 \text{ N m}^{-2} = 1 \text{ bar} = 1/1.0132 \text{ atm} = 0.987 \text{ atm.}$) Note also that smaller bubbles have much lower vapour pressures even though they require much higher internal pressures for their maintenance.

2.5.2 $d[2\gamma/r] = [RT/V^\prime] dp \gamma p^0 - dp^\prime$

$$
\frac{2\gamma}{r} = \frac{RT}{V^\prime} \left[\ln p^0\right]_{\gamma} - [p^\prime - p^0].
$$

For $r = 5 \times 10^{-9}$ m the error in $\ln p^0 p^\prime$ is $\gamma (p^0 - p) / RT$ where we can assume $p^\prime$ is approximately given by : $\ln p \gamma p^0 = [2 \times 73 \times 10^{-3} \times 18 \times 10^{-6}]/[5 \times 10^{-9} \times 8.314 \times 291] = 0.217$.

$p^\prime = 1.242p^0$ so that the error is $[18 \times 10^{-8} - 0.242 \times 1.013 \times 10^5]/8.314 \times 298 = 1.78 \times 10^{-4}$.

For the vapour pressure of the drop the corrected value of $\ln p \gamma p^0 = 0.217 + 0.000178 = 0.2172,$

S2.7
and \( p'p^0 = 1.2426 \). The correction is of order 1 in 2000 or 0.05\% at most.

2.5.3 Using equation (2.5.8) with \( \gamma \) referring to the vapour and \( \gamma' \) to the liquid, (i.e. a bubble inside a liquid):

\[
(\bar{S}'' - \bar{S})dT - \bar{V}'' dp'' = 0 \quad \text{since} \quad dp' = 0 \quad \text{(external pressure is const.)}
\]

Also \( dp'' = d(2\gamma/r) \) from eqn. (2.5.6) and

\[
\bar{S}'' - \bar{S} = \Delta \bar{S} = \frac{\Delta H_{\text{vap}}}{T} = \frac{a}{T} - b
\]

Therefore \( (aT - b) dT = V'' dp'' = [RT/p'] dp'' \).

\[
\int \left( \frac{a}{T^2} - \frac{b}{T} \right) dT = \int \frac{R dp''}{p'} = \left[ -\frac{a}{T} + b \ln T \right]_{T_0}^{T} = RT \ln \frac{P''}{P_0''}
\]

But \( p'' = p' + 2\gamma/r \) and \( P_0'' = p'' \). So \( a \left[ 1/T_0 - 1/T \right] - b \ln T/T_0 = RT \ln (1 + 2\gamma/rp') \)

2.5.4 There are several possible procedures. Since \( \Delta H_{\text{vap}} \) is given at different \( T \) values one can eliminate \( a \) and \( b \) by linear regression and obtain \( \Delta H_{\text{vap}} = (60788 - 54.637) \) J mol\(^{-1}\). (This is, incidentally, very different from the expression given by Defay et al. which is \( \Delta H_{\text{vap}} = 50560 - 27.225T \)). Then using the data for \( r = 10^{-7} \) m for example:

60788(1/373 - 1/449) - 54.63 \( \ln (449/373) = 8.31 \ln (1+2\times39.1/1.01\times10^8 r) \) we find \( r = 1.077 \times 10^{-7} \) m. A value of \( T = 452 \) K gives \( r = 1.004 \times 10^{-7} \) m in this relation.

**Exercises.** 2.7.1. Adamson (1976, p.10) defines the capillary constant, \( a \), for the rise of liquid in a capillary as \( a^2 = 2\gamma/ \rho_1 - \rho_\gamma \) g. For the approximate eqn (2.7.1) \( a^2 = rh \). The more exact analysis, taking account of the true curvature of the surface gives (Adamson 1976), p. 13):

\[
a^2 = r \left( \frac{h}{3} + 0.1288 \frac{L^2}{h} + 0.1312 \frac{L^3}{h^2} \ldots \right)
\]

S2.8
Show that the second term in the brackets takes account of the weight of the meniscus, assuming it is hemispherical. What is the percentage error in $\gamma$ using eqn (2.7.1) for $r = 1$ mm and $h = 14$ mm?

2.7.2 Consider an idealized model of a porous medium consisting of random close-packed spheres of equal radius, $R'$. Estimate the minimum pore radius, $r$, in terms of $R'$. Hence estimate the order of magnitude of the capillary rise expected in such a packed bed if $R' = 100$ $\mu$m, 10 $\mu$m and 1 $\mu$m respectively. (Note that $r$ depends somewhat on the manner of packing but only very approximate results are required.)

2.7.3(a) The pore size distribution in a microporous solid can be determined by measuring the volume, $V$, of mercury which can be forced into the pores as a function of pressure. Suppose that the (volume) distribution function for particle radius is $D(r)$, so that $dV = D(r) dr$ where $dV$ is the volume of pores of radius between $r$ and $r - dr$. Use the Young-Laplace equation to show that

$$D(r) = \frac{1}{r} \frac{dV}{d\ln p}$$

where $p$ is the pressure in the mercury. (Adamson 1976, p. 529; 1997, p.578.)

(b) Given the data in the table below. [Pressure ($P$ in psi) and Volume of mercury penetrating ($V$ in cm$^3$) in a mercury porosimetry measurement. Sample mass = 0.493 g; sample density = 3.52 g cm$^{-3}$; Apparent sample volume (including pores) = 0.344 cm$^3$. Density of mercury = 13.55 g cm$^{-3}$]

<table>
<thead>
<tr>
<th>$P$ (psi)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>500</th>
<th>700</th>
<th>1000</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$ (cm$^3$)</td>
<td>0.028</td>
<td>0.032</td>
<td>0.038</td>
<td>0.046</td>
<td>0.056</td>
<td>0.072</td>
<td>0.096</td>
<td>0.148</td>
<td>0.166</td>
<td>0.174</td>
<td>0.178</td>
</tr>
</tbody>
</table>

Plot the pore size distribution (i.e. $D(r)$) as a function of $r$, assuming the pores are cylindrical. (You may assume that $\gamma_{Hg} = 473$ dyne cm$^{-1}$ and the contact angle is 130°.) Estimate the total pore volume by integrating under an appropriate curve and compare this with the value obtained from the mass/density data.

2.7.4 Calculate the cohesive force $f^*$ between two rigid, contacting particles of radius $R' = 1$ $\mu$m, in an atmosphere of water vapour at 20°C and a relative humidity of 90 per cent. Also estimate $r$ (the curvature of the liquid meniscus) in this case and show that $r << x << R'$. Repeat the calculation for $R' = 0.05$ $\mu$m. Imagine a string of such particles dangling in moist
air with the upper one fixed in position. The only cohesive force between the particles is that due to the capillary condensed water. How many particles could be supported before the string is broken? (Assume \( \rho_s = 2.8 \text{ g cm}^{-3} \), and \( R' = 1 \mu\text{m} \) or 0.05 \( \mu\text{m} \) as before).

2.7.5 An adsorption isotherm for \( \text{N}_2 \) adsorption at 77 K on Wonkavite - a highly porous (and nutritionally worthless) children's confection is shown in Fig. 2.7.7. Estimate the pore diameter and pore volume per unit surface area. The density of liquid \( \text{N}_2 \) is \( -1 \times 10^3 \text{ kg m}^{-3} \) and the surface tension of the liquid \( \text{N}_2 \)-air interface is \( 2 \times 10^{-2} \text{ J m}^{-2} \).

2.7.6 Establish equations 2.7.11 - 13.

**Solutions** 2.7.1 Volume of meniscus = \( \pi r^2 \cdot r - 2 \pi r^3/3 = \pi r^3/3 \). Using eqn (2.7.3) we have:

\[
2\pi r \gamma \cos \theta = \pi \rho_l \cdot r g a^2 \\
\text{where } a^2 = rh = \pi \rho_l \cdot r g [h + r/3]
\]

\[-\pi \rho_l \cdot r^2 g h + \pi r^3 \rho_l g/3 \]. The first term is determined by the mass of the column of liquid without the meniscus and the second term measures the effect of the mass of the meniscus. For \( r/h = 1/14 \), we have \( a^2 = rh[1 + r^3 h - 0.1288 r^2 / h^2 + 0.1312 r^3 / h^3] \).

The correction is 0.023, i.e. a 2.3\% error.

2.7.2 If pore size = \( r \) and \( \theta = 30^\circ \) (by symmetry) then \( R'[R + R'] - \cos \theta = \sqrt{3}/2 \). So \( r = [2\sqrt{3} - 1] R' \)

\[
R' = 0.1547 \mu\text{m} \\
r = 15.47 \mu\text{m} \\
h = 0.95 \text{ m}
\]

(See eqn (2.7.1) where \( h = 2 \times 72 \times 10^{-3} / (10^3 \times 9.81 \text{ m} \) for water.)

2.7.3 (a) From the Young - Laplace equation: \( p^\beta - p^\alpha = 2 \gamma \cos \theta/r = p^\beta \) (hydrostatic pressure in the mercury). We can assume that \( \gamma \) and \( \cos \theta \) are constant and hence \( p^\beta seller = \text{constant or } r \cdot dp^\beta + p^\beta dr = 0 \). Now \( D(r) = dV/dr = (dV/d\rho)(d\rho/dr) = (dV/d\rho)(-p/r) = (1/r) [dV/d\ln \rho] \). (Defining \( dV \) as increasing when \( r \) decreases allows us to drop the negative sign.)

Given \( V \) as a function of \( \rho \) we would plot \( V \) against \( \ln \rho \), estimate \( (dV/d\ln \rho) \) at each \( \rho \) and, since
\( r = 2 \gamma \cos \theta / p \), use the \( p \) value to identify \( r \). This gives \( dV/d\ln p \) at various \( r \) from which \( D(r) \) can be estimated as a function of \( r \). In the table, the values of \( (dV)/d\ln p \) have been estimated by the less effective procedure of using the ratio of the differences: \( (\Delta V/\Delta \ln p) \).

<table>
<thead>
<tr>
<th>( p(\text{p.s.i.}) )</th>
<th>( \ln p )</th>
<th>( \text{Vol}(\text{cm}^3) )</th>
<th>( dV/d\ln p )</th>
<th>( r/\text{nm} )</th>
<th>( 10^6 D(r) )</th>
<th>( 10^3 rD(r) )</th>
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<td>0.1018</td>
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<td>272.7</td>
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<td>0.0536</td>
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<td>0.166</td>
<td>0.0224</td>
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<tr>
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<td>6.908</td>
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<td>0.0058</td>
<td>44.3</td>
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<td>14.10</td>
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<tr>
<td>2000</td>
<td>7.601</td>
<td>0.178</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( n(\text{m}) = 2 \gamma \cos \theta / p = 2 \times 473 \times 10^{-3} \times \cos 130^\circ / [p(\text{p.s.i.}) \times 1.01 \times 10^{-5} / 14.7] \) since 1 atm = 14.7 p.s.i.

So \( r(\text{nm}) = 8850/2p(\text{in p.s.i.}) \).

Since \( dV = rD(r) \, d\ln p \) then \( V = \int rD(r) \, d\ln p \). Plot \( rD(r) \) against \( \ln p \) and determine the total area under the curve (\( \text{cm}^3 \)).

Area = 144 squares with each of area \( 10^{-3} \text{ cm}^3 \) so Total volume = 0.144 \( \text{ cm}^3 \). Apparent sample volume = 0.344 \( \text{ cm}^3 \). Density = 3.52 \( \text{ g cm}^{-3} \). Volume of solid = 0.493/3.52 = 0.140 \( \text{ cm}^3 \) so volume of pores = 0.204 \( \text{ cm}^3 \).

Normal procedure would be to assume that this is the true volume and to correct all volumes in the ratio 0.204/0.144. (The discrepancy could come from a number of sources - including our crude methods of estimating \( dV/d\ln p \) and \( D(r) \) for each \( r \), as well as the absolute error in \( r \) due to \( \gamma \) and \( \cos \theta \) varying.)

\[ 2.74 \, F = 2\pi R \gamma = 2\pi \times 72 \times 10^{-3} \times 10^{-6} = 4.25 \times 10^{-7} \text{ N for } R' = 1 \mu \text{m}, \text{ and } F = 2.262 \times 10^{-8} \text{ N for } R' = 0.05 \mu \text{m}. \]

\( \dot{r} \) is given by the Kelvin eqn. with \( \rho \rho' = 0.9 \) so \( \dot{r} = -2 \times 72 \times 10^{-3} \times 18 \times 10^{-6} \\/(8.31 \times 293 \times \ln 0.9) = 1.01 \times 10^{-8} \text{ m} = 10 \text{ nm.} \)

S2.11
Also \( x = \sqrt{(2R \gamma^\prime)} = 3.2 \times 10^{-6} \text{ m} \) for \( R^\prime = 0.05 \mu\text{m} \) and so \( r < x < R^\prime \) (but only just).

For \( R^\prime = 1 \mu\text{m} \) \( x = 1.42 \times 10^{-7} \text{ m} = 0.142 \mu\text{m} \). \( r << x < R^\prime \).

If there are \( n \) particles in the string then the downward force is (for \( R^\prime \) in m) \( 4\pi R^\prime^2 \rho \gamma \nu/3 = 1.15 \times 10^5 R^\prime^3 n \) and this needs to be less than \( F \).

For \( R^\prime = 1 \mu\text{m} \) \( n < 4.52 \times 10^{-7}/1.15 \times 10^{-13} = 4 \times 10^6 \). For \( R^\prime = 0.05 \mu\text{m} \) \( n < 1.5 \times 10^6 \). This calculation brings home the enormous magnitude of these forces.

2.7.5 The very steep rise which occurs at \( \rho / \rho_{\text{sat}} = 0.5 \) is presumed to be due to capillary condensation. Using eqn (2.5.14) we have:
\[
\ln (\gamma^\prime) = -2\gamma V^\prime / rRT
\]

with \( V^\prime = 0.028 / 10^3 \) so \( r = 2 \times 2 \times 10^{-2} / 0.028 \times 10^{-3} / (8.31 \times 77 \text{ ln 2}) = 2.5 \times 10^{-9} \text{ m} = 2.5 \text{ nm} \). (This is so small that the assumption of constant \( \gamma \) is suspect.)

**Volume of pores:** When the pores are filled the relative adsorption \( (\rho / \rho_{\text{sat}}) = 0.65 \) \( = 0.65 \text{ kg of N}_2 \) per kg of solid. Volume of pores = \( 6.5 \times 10^{-4} \text{ m}^3 \) per kg. Monolayer coverage occurs at \( -0.45 \text{ kg N}_2 \) per kg of solid, i.e. \( 4.5 \times 10^{-4} \text{ m}^3 \) of \( \text{N}_2 \) per kg of solid. If the \( \text{N}_2 \) molecule is 0.5 nm in diameter this corresponds to an area of \( 9 \times 10^{-5} \text{ m}^2 \). The surface area of the solid is then 900 \( \text{ m}^2 \) per g. Volume of pores = \( 6.5 \times 10^{-4} / 9 \times 10^{-5} \text{ m}^3 \) per \( \text{ m}^2 \) of solid = \( 7.2 \times 10^{-10} \text{ m}^3 / \text{ m}^2 \)

2.7.6 From eqn. (2.7.9) and (2.7.10)

\[
dA_{\text{SL}} = \left( \frac{\phi}{1 - \phi} \rho_A A_p \right) dV_L
\]

and from (2.7.8)

\[
F = \left[ (\gamma_{SL} - \gamma_{SV}) \frac{\phi}{1 - \phi} \rho_A A_p + \Delta \rho g h \right] dV_L
\]

When \( dF = 0 \)

\[
(\gamma_{SL} - \gamma_{SL}) \phi \rho_A A_p / (1 - \phi) = \Delta \rho g h_{\text{eq}}
\]

\[
\gamma_{LV} \cos \theta_c \phi \rho_A A_p / (1 - \phi) = \Delta \rho g h_{\text{eq}}
\]

\[
\therefore h_{\text{eq}} = \gamma_{LV} \cos \theta_c \frac{\phi \rho_A A_p}{(1 - \phi) \Delta \rho g} = \frac{2 \gamma_{LV} \cos \theta_c}{\Delta \rho g r_{\text{cap}}}
\]

where \( r_{\text{cap}} = 2(1 - \phi) / (\phi \rho_A A_p) \)

S2.12
Exercises. 2.8.1 Establish eqn (2.8.8) using the fact that
\[ \mu_f(p^*) = \mu_i^0 + \int_{p^o}^{p^*} \beta \text{d}p \]
at constant temperature. \( \mu_i^0 \) is the standard chemical potential of the liquid at pressure \( p^0 \), which can be taken as the equilibrium vapour pressure over a flat surface at the temperature in question. \( V^* = v_i \) is the molar volume of the liquid.

2.8.2 Verify eqn (2.8.12).

2.8.3 Show that there is no energy barrier to growth of the nucleus for \( r > 3r_c/2 \) (Fig. 2.8.1).

Solutions 2.8.1 From (2.8.5) \( (\Delta F)_{T,V} = n \left[ \mu_i(p) - \mu_g(p) \right] - V^* (p^* - p) + \gamma A \).

The standard state for the liquid is the pure liquid in equilibrium with its vapour and so \( \mu_i^0 = \mu_g(p^0) = \mu_g^0 + RT \ln (p^0/1 \text{ atm}) \), since the standard state for an ideal gas is the gas at 1 atm pressure.

\[ \mu_f(p^*) - \mu_g(p^*) = \mu_g^0 + RT \ln \left( \frac{p^0}{1 \text{ atm}} \right) + \int_{p^0}^{p^*} \beta \text{d}p - \left[ \mu_g^0 + RT \ln \left( \frac{p^0}{1 \text{ atm}} \right) \right] \]
\[ = RT \ln \frac{p^0}{p^*} + V^*(p^* - p^0) \]

assuming that the liquid is incompressible over the range \( p^* > p > p^0 \). Substituting this in 2.8.5 and using \( V^* - n V^* \) (overline) gives 2.8.8.

2.8.2 From eqn (2.8.7):
\[ \Delta F_{\text{max}} = \Delta F_{\text{init}} = \frac{4\pi r_c^2 \gamma}{3} \quad \text{and} \quad r_c = \frac{2V^*}{RT \ln (p'/p^o)} \quad \text{by (2.8.11)} \]

S2.13
2.8.3

i.e. when $r = 3V \rho \gamma (RT \ln (p/p^0)) = 3r_e/2$. The function $(\Delta f)_{\gamma, r}$ is zero for $r = 0$, rises to a

$$\Delta f_{\text{max}} = \frac{4\pi}{3} \left[ \frac{4\gamma}{RT \ln \left( \frac{p^*}{p^0} \right)} \right]^2 = \frac{16\pi^3 M^2}{3 p_i^2 [RT \ln (p^* / p^0)]^2}$$

where $\bar{V} = M / p_i$,

$$(\Delta f)_{\gamma, r} = \frac{4\pi r^3}{3 \bar{V}} \left[ RT \ln \left( \frac{p^*}{p^0} \right) \right] + 4\pi r^2 \gamma$$

$$= 0 \quad \text{when} \quad \frac{rRT \ln (p^* / p^0)}{\bar{V}} = \gamma$$

maximum at $r = r_e$ and then decreases to zero again when $r = 3r_e/2$. (Fig. 2.8.1).

---

**Exercises.**

2.10.1 The volume of a spherical cap (such as that shown in Fig. 2.10.4) is given by $V = \pi h (a^2 + h^2)/6$ and its upper surface area is $\pi (a^2 + h^2)$. Use these relations to establish eqns (2.10.19) and (2.10.20).

2.10.2 Consider a drop of liquid sitting on a solid surface as in Fig. 2.10.4. If the drop is small enough it forms a spherical cap. Use the equation obtained in Exercise 2.10.1 to show that if the drop is in (stable or unstable) equilibrium then $\gamma_{SV} = \gamma_{SL} = \gamma_{LV} \cos \theta$. (This is, of course, just a special case of the argument leading to eqn (2.10.18).)

2.10.3 Use eqn (2.10.18) to show that if $\gamma_{13} > \gamma_{12} + \gamma_{23}$ then the drop will spontaneously spread. Show also that, no matter what the initial contact angle, if $\gamma_{13} < \gamma_{12} + \gamma_{23}$ the drop will move in such a way as to establish, at equilibrium, a contact angle given by the Young equation.

2.10.4 Consider the (two-dimensional surface represented by the) curve shown in Fig. 2.10.6. $P$ is a point on the curve and $\theta$ is the tangent angle ($-\tan \theta = dz/dx$) at $P$ as shown. $Q$ is a neighbouring point, an infinitesimal distance $ds$ along the curve in the direction shown. Show that the radius of curvature at $P$ is given by $1/r = d\theta/ds$ and, in Cartesian coordinates:

$z' [1 + z'^2]^{-3/2}$ where $z' = dz/dx$ and $z'' = d^2z/dx^2$.

2.10.5 Suppose Fig. 2.10.6 represents the meniscus of an infinite air-liquid interface
under gravity at a vertical plane wall at \( x = 0 \). The height of the interface \( z \) at distance \( x \) from the wall is measured relative to the flat interface (\( z = 0 \)) at \( x = \infty \). Show that \( z(x) \) satisfies: \( \gamma/r = \rho g z \) where \( r \) is the radius of curvature of the interface at \((x, z)\). Using the result of the previous exercise show that the tangent angle \( \theta \) at \((x, z)\) is given by

\[
\cos \theta = 1 - (1 - \rho g z^2/2\gamma).
\]

[Hint - use the result \( z \left(1 + z^2\right)^{3/2} = d \left(1 + z^2\right)^{1/2} \)/dz where \( z' = dz/dx \) and \( z'' = d^2z/dx^2 \).]

If the wall is wetting (i.e. the contact angle as measured through the liquid is zero) show that the meniscus height at the wall is \( z = (2\gamma/\rho g)^{1/2} \). (This is called the 'capillary constant' or 'capillary length'.)

2.10.6 (a) Setting the l.h.s of eqn (2.10.14) to zero provides the solution to the zero-pressure-difference-surface illustrated in Fig. 2.2.5b. Show that the solution to the resulting differential equation is \( a \sin \theta = (a \text{ constant}) \) where \( \tan \theta = dz/dx \).

(b) The zero-gravity surface (corresponding to small drops of high \( \gamma \) and/or low density) is obtained by setting the l.h.s of eqn (2.10.14) equal to a constant (i.e. assuming that the variation in \( z \) is unimportant). Show that in this case the solution to the differential equation is \( a/\sin \theta = (a \text{ constant}) \). Prove that this equation is satisfied by a spherical surface.

2.10.7. Establish equations 2.10.22-24.

**Solutions**

2.10.1 \( V = \pi h(3a^2 + h^2)/6; \quad A_{LV} = \pi(2a + h) \). We eliminate \( h \) and \( a \) from these equations using the fact that \( h = r \cos \theta = r \) or \( h = r(1 - \cos \theta) \) and

\[
a^2 = r^2 - (r \cos \theta)^2 = r^2(1 - \cos^2 \theta).
\]

Then

\[
V = \frac{\pi r(1 - \cos^2 \theta)}{6} [3r^2(1 - \cos^2 \theta) + r^2(1 - \cos^2 \theta)]
\]

\[
= \frac{\pi r^3}{3}(1 - \cos \theta)^2(2 + \cos \theta)
\]

and

\[
A = \pi[r^2(1 - \cos^2 \theta) + r^2(1 - \cos^2 \theta)] = 2\pi r^2(1 - \cos \theta).
\]

2.10.2 The total Helmholtz energy of the surface regions in the system is:

\[
F^0 = \gamma_{LV}A_{LV} + \gamma_{LS}A_{LS} + \gamma_{SV}A_{SV} = \pi \gamma_{LV}(a^2 + h^2) + \pi a^2 \gamma_{LS} + (A - \pi a^2) \gamma_{SV}
\]

where \( A \) is the area of the solid base. The volume of the drop \( V_I = \pi h(3a^2 + h^2)/6 \) is constant so \( dV_I = 0 = \)

S2.15
\[ \frac{\pi (3a^2 + h^2)}{6} dh + \pi h (6a \, da + 2dh) \] so that \[ dh = \frac{-[2ah(a^2 + h^2)]}{da}. \] Also \( \cos \theta = 1 - \frac{h}{r} \) and \( r = \frac{(a^2 + h^2)}{2h} \) so \( \cos \theta = \frac{(a^2 - h^2)}{(a^2 + h^2)} \).

Now consider a small increase in \( a \) at constant volume if \( F \) is at a stationary value (i.e. a maximum or minimum).

The \( \frac{dF}{da} = 0 = 2\pi \gamma_{LV} a + 2\pi \gamma_{LV} h dh/da + 2\pi \gamma_{SV} a - 2\pi a \gamma_{LV} \). Substituting and rearranging gives the desired result.

2.10.3. This is just the spreading coefficient, \( S \). If \( \gamma_{13} > \gamma_{12} + \gamma_{23} \) then \( S \) is positive and the oil will spread spontaneously. From equation 2.10.18, at equilibrium \( \cos \theta = (\gamma_{13} - \gamma_{12})/\gamma_{23} \). The limiting situation is when \( \theta = 0 \) so \( \cos \theta = 1 \) and then \( \gamma_{13} = \gamma_{23} + \gamma_{12} \). That is when spreading is just possible. If \( \gamma_{13} < \gamma_{12} + \gamma_{23} \) then \( \cos \theta < 1 \) and the oil droplet has a defined contact angle with the water. If the situation is not at equilibrium it will change in such a way as to establish equilibrium when \( \frac{dF}{dA_{12}} = 0 \) which is when Young's equation is obeyed.

If \( \gamma_{13} > \gamma_{12} + \gamma_{23} \) then \( \cos \theta > 1 \) which is impossible. This is the situation when spreading occurs.

2.10.4 Angle \( \text{POQ} = \theta \) (as can be seen from the angle sum of the two quadrilaterals.) Then \( ds = r \, d\theta \) or \( 1/r = d\theta /ds \). Also \( dx /ds = \cos (\pi - \theta) = -\cos \theta \). Now \( 1/r = (d\theta /dx) \, (dx /ds) \) and \( dx /ds = -\tan \theta \).

so \( \frac{d^2z}{dx^2} = -\frac{d tan \theta}{dx} = -\sec^2 \theta \, d\theta /dx \). So \( d\theta /dx = -\sec^2 \theta \, d^2z /dx^2 \).

1/r = -\cos^2 \theta \, d^2z /dx^2 . (-\cos \theta) = \frac{[d^2z/dx^2]}{sec^2 \theta} \). But \( \sec^2 \theta = 1 + \tan^2 \theta \) = 1 + (dz /dx)^2 and so \( 1/r = [d^2z/dx^2]/[1 + (dz/dx)^2]^{3/2} \).

2.10.5 From the Young -Laplace equation, the pressure drop across the curved interface is \( \gamma (1/r_1 + 1/r_2) = \gamma /r \) (since \( r_2 \to \infty \)) and this is equal to the hydrostatic pressure at height \( h \) (= z)
above the base line, i.e. \( \gamma r = \rho g z \).

Now, from exercise (2.10.4)

\[
\frac{1}{r} = \frac{d^2 z}{dx^2} \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^{3/2} = \frac{d}{dz} \left[ 1 + \tan^2 \theta \right]^{3/2} = \frac{d \cos \theta}{dz} = \frac{\rho g z}{\gamma}
\]

So

\[
\int_{-1}^{\cos \theta} d \cos \theta = \frac{z \rho g z}{\gamma} \quad \text{since} \quad \theta = \pi \quad \text{when} \quad z = 0
\]

Hence \( \cos \theta = -[1 - \rho g z^2/2 \gamma] \). If the liquid wets the wall then \( \theta = \pi/2 \) so \( \cos \theta = 0 \) and hence \( z = [2 \gamma/\rho g]^k \).

2.10.6 The zero gravity solution

From equation (2.10.14):

\[
z'' + (z' a) \left[ 1 + z'^2 \right] = 0 \quad \text{and} \quad \tan \theta = z'
\]

so \( z'' = d \tan \theta /da = \sec^2 \theta \, d \theta /da - [1 + z'^2] d \theta /da \). Therefore \( d \theta /da + a^{-1} z' = 0 \)

so \( d \theta /da = - \tan \theta /a \) or \( \cos \theta \, d \theta /\sin \theta = - da/a \) or \( d \sin \theta /\sin \theta = - da/a \).

\( \ln \sin \theta = - \ln a + k \). i.e. \( \sin \theta = k/a \) or \( a \sin \theta = k \) a constant.

(b) The zero gravity surface. From eqn. (2.10.14):

\[
z'' + a^{-1} z \left[ 1 + z'^2 \right] = k_1 \left[ 1 + z'^2 \right]^{3/2} \quad \text{or} \quad \sec^2 \theta \, d \theta /da + a^{-1} \tan \theta \, \sec^2 \theta = k_1 \, \sec^2 \theta
\]

or \( \cos \theta \, d \theta /da + \sin \theta /a = k_1 = d \sin \theta /da + \sin \theta /a \).

\( a^{-1} d(\sin \theta) /da = k_1 \) so \( a \sin \theta = \int k_1 \, da \) and hence \( a \sin \theta = k_1 a^2/2 + k_2 \).

But \( \theta = 0 \) when \( a = 0 \) (at the highest point of the sessile drop) or \( \theta = \pi \) when \( a = 0 \) (at the lowest point of the pendant drop). So \( k_2 = 0 \) and \( \sin \theta /a = k_1 /2 \) a constant.

Note that the two terms on the RHS of eqn (2.10.14) are \( 1/r_1 \) and \( 1/r_2 \). We showed earlier [Exercise (2.10.4)] that the radius of curvature in the plane of the paper is given by

\[
\frac{1}{r_1} = \frac{d^2 z/da^2}{[1 + (dz/da)^2]^{3/2}} = \frac{\sec^2 \theta \, d \theta /da}{\sec \theta} = \frac{d \sin \theta}{da}
\]
The radius, \( r_2 \) in the other plane is obviously \( a/\sin \theta \) (see figure). (Note that for any concave axially symmetric surface, the centre of curvature in this plane must be on the median line. We can then write:

\[
1/r_2 = \sin \theta/a = \tan \theta/[\alpha \sec \theta] = (dz/da)/a[1 + (dz/da)^2]^{1/2}.
\]

In the case of the zero pressure solution these two terms are equal and opposite. In the case of the zero gravity solution the two radii are equal, giving rise to a spherical cap:

\[
1/r_1 = d\sin \theta/da = k_1/2 \quad \text{and} \quad 1/r_2 = \sin \theta/a = k_2/2.
\]

Alternatively we may take the equation for a circle: \( a^2 + (z-q)^2 = b^2 \) (with \( p \) and \( q \) constant and evaluate these two radii of curvature. Differentiating with respect to \( a \):

\[
2a + 2(z-q) \frac{dz}{da} = 0 \quad \text{so} \quad \frac{dz}{da} = -a/(z-q)
\]

and a second differentiation gives:

\[
1 + (z-q) \frac{d^2z}{da^2} + \left( \frac{dz}{da} \right)^2 = 0 \quad \text{and so} \quad \frac{d^2z}{da^2} = \frac{1}{a} \frac{dz}{da} \left[ \frac{1}{1 + (dz/da)^2} \right] + \left( \frac{dz}{da} \right)^2
\]

Thus

\[
1/r_1 = \frac{d^2z/da^2}{[1 + (dz/da)^2]^{1/2}} = \frac{1}{a} \frac{dz}{da} \frac{1}{[1 + (dz/da)^2]^{1/2}} = \frac{1}{a} \tan \theta = \frac{\sin \theta}{a}.
\]

and the same result applies to \( 1/r_2 \). The profile for the zero pressure surface is: For \( z = 0 \), \( a = R_2 \) and \( \theta = \pi/2 \) so \( k' = a \sin \theta = R_2 \).
2.10.7 The second term in equation (2.10.21) when Young's eqn. is obeyed becomes:
\[ \gamma_{L,V} \pi r^2 (1 - \cos \theta) \theta - \gamma_{L,V} \pi r^2 (1 - \cos^2 \theta) \cos \theta = \gamma_{L,V} \pi r^2 (1 - \cos \theta) [2 - \cos \theta - \cos^2 \theta] \]
- \[ \gamma_{L,V} \pi r^2 (1 - \cos \theta)^2 (2 + \cos \theta) \] which gives eqn 2.10.22 immediately.

\[ (\Delta F)_{T,V} = \pi r^2 (1 - \cos \theta)^2 (2 + \cos \theta) \left[ \gamma_{L,V} - \left(\frac{r}{3V_L}\right)RT \ln \frac{p}{p^0} \right] \] and substituting Kelvin's eqn:

\[ (\Delta F)_{T,V} = \pi r^2 (1 - \cos \theta)^2 (2 + \cos \theta) \left[ \gamma_{L,V} - 2 \gamma_{L,V}/3 \right] = \left(\frac{\pi r^2}{3}\right) \gamma_{L,V} (1 - \cos \theta)^2 (2 + \cos \theta) \]

which is eqn (2.10.23 and 2.10.24).
Solutions

Chapter 3

Exercises 3.1.1 Consider a spherical particle settling under gravity according to eqn (3.1.1). Show that during the period before it reaches terminal velocity its equation of motion is:

\[ \frac{dw}{dt} = pg - Gu \]

where \( \rho = (\rho_k - \rho_l)/\rho_k \) and \( G = 9\eta/2\rho_k r^2 \). Hence show that \( u = (pg/G)(1 - \exp(-Gr)) \) during this period. How long does it take for a particle of radius 1 \( \mu \)m and density 3 \( \times 10^3 \) kg m\(^{-3}\) to reach 99 per cent of its terminal velocity in water (density = 10\(^3\) kg m\(^{-3}\), viscosity = 10\(^{-3}\) Nm\(^{-2}\) s)? Repeat the calculation for a radius of 0.1 \( \mu \)m and 0.01 \( \mu \)m. (Allen 1975, p.158).

3.1.2 A suspension of silica particles (\( \rho_s = 2.8 \) g cm\(^{-3}\)) in water is allowed to settle in a cylinder at 20\(^\circ\)C. Calculate the time required for a particle of 2 \( \mu \)m radius to settle a distance of 20cm, assuming it is spherical. (Take \( \eta = 10^{-2} \) g cm\(^{-1}\) s\(^{-1}\) = 1 centipoise.) Convert the data to SI units, and repeat the calculation.

3.1.3. Show that for colloidal particles dispersed in a liquid, the equilibrium number of particles, \( N \), at a height, \( h \) above a reference level, \( h_0 \) is given by:

\[ N = N_0 \exp\left[-\frac{(m - m') g (h - h_0)}{kT}\right] \]

where \( N_0 \) is the number of particles at height \( h \) and \( m' \) is the mass of fluid displaced by a particle of mass \( m \) (\( k \) is the Boltzmann constant).

3.1.4 Svedberg (1928, p.101) gives the following table of Westgren’s date for the number of particles at different heights in a gold sol at sedimentation equilibrium under gravity.

<table>
<thead>
<tr>
<th>Height (( \mu )m)</th>
<th>0</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>889</td>
<td>692</td>
<td>572</td>
<td>426</td>
<td>357</td>
<td>253</td>
</tr>
<tr>
<td>Height</td>
<td>600</td>
<td>700</td>
<td>800</td>
<td>900</td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>Number</td>
<td>217</td>
<td>185</td>
<td>152</td>
<td>125</td>
<td>108</td>
<td>78</td>
</tr>
</tbody>
</table>

Assume the particles have radius 21 nm and density 19.3 g cm\(^{-3}\) and the temperature is 20\(^\circ\)C. Estimate \( k \) from the equation derived in Exercise 3.1.3 and then calculate \( N_j \) assuming \( R = 8.31 \) JK\(^{-1}\) mol\(^{-1}\). Repeat the calculation with a radius of 22 nm and note how sensitive the answer is to this variable.

3.1.5 The time taken for a particle to reach its terminal velocity under gravity is about \( S/G \) (Exercise 3.1.1). Show that the sedimentation coefficient, \( S \), is also an approximate measure

\[ S \approx \frac{3}{t} \]
of this time.

3.1.6 In a sedimentation equilibrium experiment, Svedberg found the following concentration 
(C)-depth (x) profile for carboxyhaemoglobin:

<table>
<thead>
<tr>
<th>x(cm)</th>
<th>4.61</th>
<th>4.56</th>
<th>4.51</th>
<th>4.46</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(%)</td>
<td>1.220</td>
<td>1.061</td>
<td>0.930</td>
<td>0.832</td>
</tr>
</tbody>
</table>

The rotor speed was 8710 r.p.m. and the temperature was 20.3°C. Take the density of the water as 0.9988 g cm⁻³ and that of the dry protein as 1.338 g cm⁻³ and estimate the molar mass of the protein, assuming that the molecules sediment as individual particles.

3.1.7 An informal demonstration of the reasonableness of eqn (3.1.14) can be given by balancing the sedimentation force, \((m - m' - \rho_r \rho_s)\omega^2 x\), against the driving force for the diffusion process (eqn (1.5.11)). Derive eqn (3.1.14) by this method; then derive eqn (3.1.15).

3.1.8 Calculate the centrifugal acceleration at a distance of 7 cm from the axis of an ultracentrifuge rotor travelling at 20,000, 40,000 and 60,000 r.p.m. and compare this with the gravitational acceleration, g.

---

**Solutions**

3.1.1 \[ \frac{du}{dt} = g - m ' g / m - f_r / m \]. But \( m ' = \rho_r \rho_s \) and \( f_r / m = (6 \pi \eta r_w / 4 / 3) \pi r^3 \rho_s \).

Therefore \[ du / dt = \rho g - Gu \] where \( \rho = (\rho_s - \rho_s) / \rho_s \) and \( G = 9 \eta / (2 \rho_s r^2) \)

\[ t = \int \frac{du}{\rho g - Gu} = - \frac{1}{G} \ln(\rho g - Gu) + \text{a constant.} \]

But \( u = 0 \) when \( t = 0 \) so the constant = \( - \ln(\rho g) \).

Then \( -Gu = \ln[1 - (Gu / \rho g)] \) or \( u = (\rho g / G)[1 - \exp(-Gu)] \).

For \( u = 0.99 \ u \), we require \( \exp(-Gu) = 0.01 \) (since \( u = \rho g / G \)).

Therefore \( t = G^{-1}(- \ln(0.01)) = 4.605 / G \).

\( t = 3.1 \ \mu s \) for \( r = 1 \ \mu m \); \( t = 31 \ \text{ns} \) for \( r = 0.1 \ \mu m \) and \( 0.31 \ \text{ns} \) for \( r = 0.01 \ \mu m \).

3.1.2 \[ u = 1.57 \times 10^{-3} \ cm \ s^{-1}; \quad t = 3 \ \text{hrs 32 min.} \]

3.1.3 From \( d (\ln c) = -M c / RT \). The analogous expression for particles in a fluid would be:

\[ \frac{\Delta \ln c}{\Delta t} = -M c / RT \]
\[
\frac{d(\ln N)}{dt} = \frac{-(m-m')g dh}{kT} \quad \text{or} \quad N = N_0 \exp \left( \frac{-(m-m')g(h-h_0)}{kT} \right)
\]

3.1.4 Values of \(-\ln (N/N_0)\) plotted against \((h - h_0)\) should be linear with a slope of 
\(+\frac{(m-m')g}{kT}\).

<table>
<thead>
<tr>
<th>(h/\mu\text{m})</th>
<th>0</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\ln (N/N_0))</td>
<td>0.00</td>
<td>0.25</td>
<td>0.44</td>
<td>0.74</td>
<td>0.91</td>
<td>1.26</td>
</tr>
<tr>
<td>(h/\mu\text{m})</td>
<td>600</td>
<td>700</td>
<td>800</td>
<td>900</td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>(-\ln (N/N_0))</td>
<td>1.41</td>
<td>1.57</td>
<td>1.77</td>
<td>1.96</td>
<td>2.10</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Regression gives a slope of \(2.147 \times 10^3 \text{ m}^{-1}\), intercept at 0.05563.
That means \(k = 18.3 \times 10^3 \times (4\pi \times (21 \times 10^{-9})^3 \times 9.81) / (3 \times 2147 \times 293) = 1.107 \times 10^{-23} \text{ K}^{-1}\).
That corresponds to \(N_A = 8.31 / k = 7.51 \times 10^{23}\).
For \(r = 22 \text{ nm}\), \(k = 1.27 \times 10^{-23}\) and \(N_A = 6.53 \times 10^{23}\) which is much closer to the accepted figure of \(6.022 \times 10^{23}\).

3.1.5 If one regarded the particle as being in free fall under gravity with an initial velocity, \(u = 0\), and a terminal velocity, \(v_t\), after time \(t\), with an acceleration \(g\), then \(v = 0 + gt\) and \(t = v/g\). But \(v/g = 2(\rho - \rho_0)r^2/9\eta = m'^2B = S\) (the sedimentation coefficient).

3.1.6 Plot \(\ln(c)\) against \(x^2\) (according to eqn 3.1.15):

<table>
<thead>
<tr>
<th>(x^2)</th>
<th>21.25</th>
<th>20.79</th>
<th>20.34</th>
<th>19.89</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ln c)</td>
<td>0.1989</td>
<td>0.0592</td>
<td>-0.0725</td>
<td>-0.1839</td>
</tr>
</tbody>
</table>

Slope = 0.2827 cm \(^2\) = \((M\omega^2/2RT)[1 + \rho_i/\rho_i] \) so \(M_i = 6.54 \times 10^4\).

3.1.7 At equilibrium in the centrifugal field, the diffusional force (eqn 1.5.14) balances the centrifugal force:

\[
\frac{kT}{c_i} \frac{dc_i}{dx} = (m-m')\omega^2 x \quad \text{so} \quad \int_{c_i}^{c_f} \frac{dc_i}{c_i} = \frac{(m-m')\omega^2}{kT} \int x \, dx
\]

\(\S\) 3.2

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Then \[ \ln(c_2/c_1) = \frac{(m - m')\omega^2}{2kT}(x_2^2 - x_1^2). \]

If \( x \) is measured from the point where \( c_i = c_0 \) then \( x_1 = 0 \) which gives eqn (3.1.14).

Substituting \( (m - m')/k = m_0[1 - \rho_1\rho_2]/M_1[1 - \rho_0\rho_1]/N_0 \) gives eqn (3.1.15).

3.1.8 Centrifugal acceleration = \( \omega^2 x \). For \( \omega = 20 \, 000 \), \( 40 \, 000 \) and \( 60 \, 000 \) RPM the corresponding accelerations are: \( 3.13 \times 10^4 \)g, \( 1.25 \times 10^5 \)g and \( 2.82 \times 10^5 \)g.

Exercises 3.2.1 Establish equation (3.2.14).

3.2.2 Draw an Argand diagram to represent the functions (3.2.31) - (3.2.33).

3.2.3 Establish eqns (3.2.31) - (3.2.33).

3.2.4 Establish eqn (3.2.34).

3.2.5 Consider a capacitor (for which \( C(\omega) = \epsilon(\omega)\omega d/d \)) subjected to an alternating voltage \( V = V_0 \cos \omega t \). The resulting current is the real part of \( I = V/Z \) where \( Z \) is the capacitive impedance or reactance and \( Z = -1/j\omega C \). (This is the a.c. analogue of Ohm’s Law.) Show that \( I = (\omega A/c) V_0[\epsilon^* \cos \omega t - \epsilon' \sin \omega t] \) where \( A \) is the capacitor plate area.

By considering the integral \( d/d\omega \int I(\omega) V(\omega) d(\omega) \) show that the power dissipated in the capacitor is entirely determined by \( \epsilon^* \):

Power dissipated per cycle = \( (\pi A/c) V_0^2 \epsilon^*(\omega) \)

whereas \( \epsilon' \) relates to the storage of electrical energy during the cycle.

3.2.6 Consider the extension of the problem treated in section 3.2.2 to include a friction (damping) term to the electron’s motion. The equation of motion will then be:

\[
\frac{m\,d^2x}{dt^2} = -k_x x - \frac{B}{d} \frac{dx}{dt} + qE(t).
\]

Take \( E = E_0 \exp(-i\omega t) \) and \( x = A \exp(-i\omega t) \) where \( A \), the amplitude of the motion, can be complex in this formulation. Verify by direct substitution in the equation of motion that:

\[
A = qE_0/[m(\omega_0^2 - \omega^2) - i\omega B].
\]

Show that \( A \) can be written in the form \( x' + ix'' \) where \( x' \) and \( x'' \) are real functions and then:

\[
x'' = qE_0 \omega B [m^2(\omega_0^2 - \omega^2)^2 + \omega^2B^2].
\]

\[ \boxed{\text{\S 3.4}} \]
3.2.7 Show that in the neighbourhood of the resonance frequency \( \omega = \omega_0 \) (Ex 3.2.6):

\[
x^* = \frac{qE_0}{2ma_0} \left[ \frac{Q}{(\omega - \omega_0)^2 + Q^2} \right]
\]

where \( Q = B/2m \). The plot of \( x^* \) as a function of \( \omega \) is called a Lorentzian distribution. It is commonly used to represent the shape of the lines in an absorption spectrum (See Fig. 5.7.4). Again it is the imaginary part of the displacement function which has the form of the absorption (dissipation) curve. Since the dipole moment is \( qx \) this measures the magnitude of the dipole moment out of phase with the field.

3.2.8 Show that if (eqn (3.2.39)):

\[
\epsilon'(\omega) = \frac{\epsilon_0 f_j}{\omega_{0j}^2 + f_j (-i\omega) + (-i\omega)^2} = \epsilon' (\omega) + i\epsilon'' (\omega)
\]

then the imaginary part \( \epsilon'' \) has exactly the same form as \( x^* \) obtained from Exercise (3.2.6). Thus eqn (3.2.39) can be expected to represent the behaviour of a bound electron moving against viscous friction in response to an applied field.

3.2.9 An electromagnetic wave of velocity \( c \) has wave vector \( k \) where \( k = \omega/c \). The wave vector in any medium is related to the medium properties by \( k^2 = \epsilon(\omega)\mu(\omega)\omega^2 \) where \( \mu(\omega) \) is the magnetic permeability of the medium. We also know that the velocity in vacuo is given by \( c_0 = (\epsilon_0 \mu_0)^{1/2} \). The refractive index, \( n \) and absorption coefficient, \( \kappa \), are defined by the relation \((n + i\kappa)\omega/c_0 = k \). Use these relations to justify equation (3.2.36) for non-magnetic materials (for which \( \mu = \mu_0 \)).

**Solutions**

3.2.1 \( x - x_0 \exp(-i\omega t) \) so \( dx/dt = -i\omega x_0 \exp(-i\omega t) \). Therefore \( d^2x/dt^2 = -\omega^2 x_0 \exp(-i\omega t) \). From eqn (3.2.7) \(-ma_0^2 \exp(-i\omega t) = -k_0 x_0 \exp(-i\omega t) + qE_0 \exp(-i\omega t) \) from which eqn (11) arises. The dividing by \( m/q \):

\[
-\omega^2 q x_0 \exp(-i\omega t) = -\omega_0^2 q x_0 \exp(-i\omega t) + (q^2 E_0/m)\exp(-i\omega t) \]

\(-\omega^2 \omega_0^2 - \omega^2 P_0 + q^2 E_0/m \) or \((\omega_0^2 - \omega^2)P_0 = \alpha_0 \omega_0^2 E_0 \) where \( \omega_0^2 = k_0/m \) & \( \alpha_0 \omega_0^2 = q^2/m \).

\[ \S 3.5 \]

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3.2.3 \( \epsilon(x) = r \exp(i\delta) = r (\cos \delta + i \sin \delta) \) where \( r = |\epsilon(x)| \).

But \( \epsilon \) = \( r \cos \delta \) and \( \epsilon \) = \( r \sin \delta \) so \( \epsilon(x) = |\epsilon(x)| \exp(i\delta) \)

where \( |\epsilon(x)| = \{ \epsilon(x)^2 + \epsilon(x)^2 \}^{1/2} \)

and \( \tan \delta = \epsilon \epsilon \)

3.2.4 \( D(r, t) = \epsilon_0 \epsilon(x) E(r, t) = \epsilon_0 |\epsilon(x)| \exp[i\delta] E(r, t) \exp(-i\omega t) \)

\( \Re D(r, t) = \Re \epsilon_0 |\epsilon(x)| \exp[i\delta] E(r) \exp(-i\omega t) = \Re \epsilon_0 |\epsilon(x)| E(r) \exp[-i(\omega t + \delta)] \)

\( = \epsilon_0 |\epsilon(x)| E(r) \cos(\omega t + \delta) \)

3.2.5 \( V = V_0 \cos \omega t = \Re[V_0 \exp(-i\omega t)] \) and \( \Im[V_0 \exp(-i\omega t)] = 0 \)

\( 1 - V/Z = \Re[V_0 \exp(-i\omega t) (-i\omega C)] = \Re[V_0 \exp(-i\omega t) (-i\omega \epsilon_0 \epsilon(x) A d)] \)

\( = \Re[-i\omega \epsilon_0 (AV_0 d) (\cos \omega t - i \sin \omega t) (\epsilon(x) + i \epsilon(x))] = \omega \epsilon_0 (AV_0 d) \sin \omega t - \epsilon(x) \sin t] \).

Power dissipated by the in-phase current = \( A \int_{-\infty}^{\infty} I(\omega t) V(\omega t) \) d\( t \).

\( = \frac{\epsilon_0 A V_0}{d} \int_{-\infty}^{\infty} \epsilon(x) \cos \omega t. V_0 \cos \omega t. d(\omega t) = \frac{\epsilon_0 A V_0^2 \epsilon(x)}{d} \int_{-\infty}^{\infty} \cos^2 \omega t. d(\omega t) \)

\( = \frac{\epsilon_0 A V_0^2 \epsilon(x)}{d} \int_{-\infty}^{\infty} \frac{1}{2} (\cos 2 \theta + 1) d(\omega t) = \frac{\epsilon_0 A V_0^2 \epsilon(x)}{d} \left[ \frac{\sin 2 \theta}{4} \right]_{0}^{\infty} = \frac{\epsilon_0 A V_0^2 \epsilon(x)}{d}. \)

Note that the out of phase current involves no dissipation.
3.2.6 \( m\ddot{x} + B\dot{x} + k_0 x = qE_0 \exp(-i\omega t) \). Assume that \( x = A \exp(-i\omega t) \) then \( \dot{x} = -i\omega A \exp(-i\omega t) \) and \( \ddot{x} = -\omega^2 A \exp(-i\omega t) = -\omega^2 x \).

Therefore \(-\omega^3 A \exp(-i\omega t) - B\omega A \exp(-i\omega t) + k_0 A \exp(-i\omega t) = qE_0 \exp(-i\omega t)\)

\[
A = \frac{qE_0}{(k_0 - m\omega^2) - i\omega B} = \frac{qE_0}{m(\omega^2_0 - \omega^2) - i\omega B}
\]

But \( \frac{1}{a - ib} = \frac{a + ib}{a^2 + b^2} \) so \( A = \frac{qE_0[m(\omega^2_0 - \omega^2) + i\omega B]}{m^2(\omega^2_0 - \omega^2)^2 + \omega^2 B^2} \)

\[= x' + ix'' \quad \text{where} \quad x'' = \frac{qE_0 B}{m^2(\omega^2_0 - \omega^2)^2 + \omega^2 B^2} \]

3.2.7 If \((\omega - \omega_0) \ll (\omega_0 + \omega)\) and \(\omega = \omega_0\) then

\[x'' = \frac{qE_0 B}{m^2(\omega - \omega_0)^2(\omega + \omega_0)^2 + \omega^2 B^2} = \frac{qE_0 B}{4\omega_0 m^2(\omega - \omega_0)^2 + \omega_0 B^2} \]

\[= \frac{qE_0}{2m\omega_0} \left[ \frac{H/2m}{(\omega - \omega_0)^2 + H^2/4m^2} \right] = \frac{qE_0}{2m\omega_0} \left[ \frac{Q}{(\omega - \omega_0)^2 + Q^2} \right] \]

where \(Q = H/2m\).

3.2.8

\[e(\omega) = \frac{f_j}{\omega^2 + jg_j(-i\omega) + (-i\omega)^2} \]

\[= \frac{f_j}{(\omega^2_0 - \omega^2) - i\omega g_j} \times \frac{(\omega^2_0 - \omega^2) + i\omega g_j}{(\omega^2_0 - \omega^2) + i\omega g_j} \]

\[= \frac{f_j(\omega^2_0 - \omega^2) + i\omega g_j f_j}{(\omega^2_0 - \omega^2)^2 + \omega^2 g_j^2} \]

\(S \geq 7\)
Written in the form $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ we would have

$$
\epsilon''(\omega) = \frac{\omega g_j f_j}{(\omega_0 - \omega^2)^2 + \omega^2 g_j^2}
$$

which is of the same form as $\chi''$ in Exercise (6),

with $qBE_d/m^2 = g_j/f_j$ and $B^2/m^2 = g_j^2$, i.e. $g_j = B/m$ and $f_j = qE_d/m$.

3.2.9 \(k = \omega/c\) and $k^2 = \epsilon(\omega)\mu(\omega)\omega^2 = \epsilon(\omega)\mu(\omega)$\ for $\mu(\omega) = 1$. And $c_0^2 = 1/\epsilon_0\mu_0$.

Also $\left(n_1 + i\kappa\right)\omega = c_0k$. So \(n_1^2 - \kappa^2 + 2in_1\kappa = c_0\epsilon(\omega) = \epsilon''(\omega) + i\epsilon'(\omega)\) which gives eqns (3.2.36) by matching real and imaginary parts.

**Exercises**

3.3.1 Describe briefly what occurs when visible light is absorbed by a particle. In what way is the energy usually stored? Why does re-radiation usually occur at a longer wavelength? When is this not the case? If re-radiation does occur at the incident wavelength is the effect on the incident beam noticeable? Why?

3.3.2 Use the definitions of $\alpha$ and $P$ from Section 3.2 to find a link between $\alpha$ and $\epsilon(\omega)$.

In a region where there is no absorption, show that

$$
\alpha = \epsilon_0 \left(n_1^2 - 1\right)/N
$$

for a collection of gas molecules of refractive index $n_1$ with $N$ molecules per unit volume. Show that this can be reconciled with eqn (3.3.4) for a condensed medium (where $N = (4\pi a^2/3)$) if $\epsilon_r$ is related to the refractive index.

3.3.3 Establish equations (3.3.9) and (3.3.10).

3.3.4 Use the standard expansions:

$$
\sin x = x - x^3/3! + x^5/5! \ldots \ldots \text{and} \cos x = 1 - x^2/2! + x^4/4! - \ldots \ldots
$$

to establish equation (3.3.15).

3.3.5 Show that the radius of gyration of a spherical particle of uniform density is related to its radius by: 

$$
a_G = \sqrt{(3/5)}a. \text{ Note that this reconciles equations (3.3.15) and (3.3.16) for a sphere.}
$$

(Hint: $a_G = \text{(moment of inertia/total mass)}^{1/2} = \left[ \frac{1}{V_0} \left\int_{V} r^2 \rho \, dV \right\right]^{1/2}$)

$$
\iint_{V} z \cdot \rho
$$

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Solutions

3.3.1 Absorbed light causes a quantum transition to an excited state (e.g. vibrational, rotational or electronic). That energy may be partly redistributed to other modes in the molecule and be degraded ultimately as heat (a radiationless transition) or it may be that only part is so redistributed and the remainder is emitted at a lower frequency.

Even if the lifetime of the excited state is short so that no redistribution occurs, the radiated light of the same frequency as the absorption is radiated in all directions and there is, even in that case, a great reduction in the intensity in the direction of the input beam.

3.3.2 From the definition of $\alpha : p = \alpha E$ (eqn 3.2.16) and $P = (\epsilon - \epsilon_0)E$ (eqn 3.2.5).

But $P = Np$ (eqn 3.2.17) = $NaE$ where $N$ is the number of molecules per unit volume.

Therefore, $\alpha = (\epsilon - \epsilon_0)/N = \epsilon_0[(\epsilon - 1)/N = \epsilon_0 n_2 - 1)/N$ from (3.2.36) in the region where there is no absorption. Writing $N^1 = 4\pi R^3/3$ gives $\alpha = 4\pi \epsilon_0 (\epsilon - 1)R^3/(\epsilon_2 + 2)$ for $\epsilon_2 = 1$.

\[
\alpha = \frac{3\epsilon_0(\epsilon - 1)}{N^m(\epsilon_2 + 2)} \quad \text{from eqn 3.3.4 and } \epsilon_2 + 2 = 3 \quad \text{so:}
\]

\[
\alpha = \frac{\epsilon_0(n_s^2 - n_0^2)}{N^p} = \frac{\epsilon_0(n_s + n_0)(n_s - n_0)}{N^p}
\]

\[
\alpha = 2\epsilon_0 n_0 (n_s - n_0)/N^p = 2\epsilon_0 n_0 (d\sigma /dN_p) = 2\epsilon_0 n_0 (M/N \Lambda)(d\sigma /dC) \text{ since } C = N^p M/N \Lambda.
\]

This is eqn (3.3.9).

Now $R(\theta) = \lambda^2 II_{10} V_s$ from (3.3.7) so

\[
R(\theta) = \frac{16\pi^2}{\lambda^4 V_s^4} \left( \frac{\alpha}{4\pi \epsilon_0} \right)^2 N \quad \text{from (3.3.3) for N scatterers}
\]

\[
= \frac{16\pi^2 N}{\lambda^4 V_s^4} \left( \frac{2n_0 M d\eta}{4\pi N \Lambda dC} \right)^2 \text{ using the result above.}
\]
\[ R(\theta) = \frac{4\pi^2 N CM n_0^2}{\lambda^4 N_A} \left( \frac{dn}{dC} \right)^2 = CKM \text{ where } K = \frac{4\pi^2}{\lambda^4 N_A} n_0 \left( \frac{dn}{dC} \right)^2 \]

The function \( P(\theta) \) must be introduced (eqn (3.3.7)) to account for the polarisation of the incident and scattered light.

### 3.3.4

\[ P(\theta) = \left\{ \sin Qa - Qa \cos Qa \right\}/(Qa)^3 \text{ form (3.3.14)} \]

Now:

\[ \sin Qa = Qa - (Qa)^3/3! + (Qa)^5/5! - \ldots \text{ and } \cos Qa = 1 - (Qa)^2/2! + (Qa)^4/4! - \ldots \]

\[ P(\theta) = \left[ \frac{3}{(Qa)^3} \left( Qa - \frac{(Qa)^3}{3!} + \frac{(Qa)^5}{5!} - \frac{(Qa)^7}{7!} + \frac{(Qa)^9}{9!} \right) \right] \]

\[ = \left[ \frac{3}{2} - \frac{1}{3.2} \right] + 3 \left[ \frac{1}{5.4.3.2} - \frac{1}{4.3.2.1} \right] (Qa)^2 \]

\[ = 1 - \frac{1}{10} (Qa)^2 \]

\[ = 1 - \frac{1}{5} (Qa)^2 \]

which is eqn (3.3.15).

### 3.3.5

Radius of gyration = (moment of inertia / total mass)\(^{1/2}\) = \( a_G \)

\[ a_G = \left[ \int \rho^2 dV \right]^{1/3} \]

\[ a_G^2 = \frac{2\pi a}{3} \]

\[ = \frac{2\pi}{3} \int_0^\pi \int_0^a r^2 \sin \theta d\theta d\phi \]

\[ = \int_0^\pi \sin \theta d\theta \int_0^a \phi d\phi \]

\[ = \frac{2\pi a^5}{5} \int_0^{\pi/2} [-\cos \theta] d\phi = \frac{2\pi a^5}{5} \int_0^{\pi/2} d\phi = \frac{4\pi a^5}{5}. \]

Therefore \( a_G^2 = 4\pi a^5/5 + 4\pi a^3/3 = 3a^2/5 \) so \( a_G = \sqrt{3/5} \) \( a. \)

\[ \wedge \]

\[ \sum_{\theta} \]

\[ \Theta \]

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Exercises. 3.4.1 Establish eqn (3.4.5) from eqn (3.4.4).

3.4.2 Establish eqn (3.4.8).

3.4.3 Show that in the stress relaxation experiment of Fig. 3.4.5
\[ S(t) = \dot{\gamma} \int_{t'}^{\infty} G(\tau) \, d\tau. \]

3.4.4 Establish eqn (3.4.10).

Solutions

\[ S(t) = \left[ \int_{t'}^{\infty} G(t-t') \dot{\gamma}(t') \, dt' \right]_0^t - \int_{t'}^{\infty} \left[ \frac{dG(t-t')}{dt'} \int_{t'}^{\infty} \dot{\gamma}(t'') \, dt'' \right] \, dt'. \]

The first term is zero because at the upper limit both parts are zero, and at the lower limit \( G(\infty) = 0 \) because the material is liquid-like. Note that in setting up the partial integration the strain in only measured from \( t \) to \( t' \). In other words, the reference state for the measured strain is the strain at time \( t \).

Then
\[ S(t) = - \int_{t'}^{\infty} \frac{dG(t-t')}{dt'} \gamma(t', t) \, dt' = - \int_{t'}^{\infty} m(t-t') \gamma(t', t) \, dt' \]

where \( m(t) = \frac{dG(t)}{dt} \) so \( m(t-t') = \frac{dG(t-t')}{dt-t'} = \frac{dG(t-t')}{dt'} \).

3.4.2

\[ S(t) = \int_{t'}^{\infty} G(t-t') \frac{\gamma}{\xi} \, dt' \quad (eqn\,(3.4.7)) \]

From Fig. 3.4.4 the integral can be replaced by the rectangular area ABCD and so

substituting \( t' = t_0 - \xi + \varepsilon \xi \):

\[ \int_3 \text{ d} \]
\[ S(t) = G[t - (t_0 - \xi + e\xi)] - \frac{\gamma}{\xi} [t_0 - (t_0 - \xi)] \]
\[ = \gamma G[t - t_0 + \xi(1 - e)] \]

So for \( t_0 = 0 \):
\[ S(t) = \gamma G[t + \xi(1 - e)] = \gamma G(t). \]

3.4.3 Note that in Eqn. (3.4.4) although \( t \) is a variable it is treated as a constant inside the integral because the integral must be evaluated for each value of \( t \) over the whole range of \( t' \) values \((-\infty < t' < t)\). In this experiment, \( \gamma (t') = \text{constant} \) for \(-\infty < t' < t_0\) and equal to zero for \( t_0 < t' < \infty \). Hence we consider the first part of the integral:

\[ S(t) = \gamma \int_{-\infty}^{t_0} G(t - t') \, dt' \quad -\infty < t' < t_0 \]

and putting \( \tau = (t - t') \) so that \( d\tau = -dt' \) and for \( t' = -\infty, \tau = \infty \) and \( t' - t_0, \tau = t - t_0 \). Then:

\[ S(t) = \gamma \int_{t_0}^{\infty} G(\tau) \, d\tau. \]

3.4.4

\[ \gamma(t) = \int_{-\infty}^{t} \mathcal{J}(t - t') \hat{S}(t') \, dt' \quad \text{eqn}(3.4.6) \]

Note that (Fig. 3.4.6) \( dS/dt \) is non-zero only in the short interval \( (t_0 - \xi) < t' < t_0 \) and it can be assumed to be approximately constant over that period and equal to \( S/\xi \). Then:

\[ \gamma(t) = \int_{t_0 - \xi}^{t} \mathcal{J}(t - t') \hat{S}(t') \, dt' \]

\[ \approx \frac{S}{\xi} \mathcal{J}[t - (t_0 - \xi + e\xi)].\xi = S\mathcal{J}(t) \]

for \( t_0 = 0 \) and times, \( t \) long compared to \( \xi \).

\[ S \approx 12 \]

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Solutions

Chapter 4

Exercise 4.2.1 Establish equations 4.2.2 and 4.2.3 using the sort of argument developed in Appendix 3.3.

Solution: From eqn (4.2.1) the rate of flow through faces ABCD, of area \( \Delta A = \Delta x_2 \Delta x_3 \) is 
\[ \rho \nu_1 (\hat{n} \cdot \Delta x_2 \Delta x_3) \] 
and since \( \hat{n} \) is in this case the unit vector in the direction of \( v_1 \) (and \( x_1 \)) it follows that 
\[ v \cdot \hat{n} = v_1 [x_1 - (\Delta x_1/2), x_2, x_3] \] (i.e. \( v_1 \) evaluated at the centre of the face ABCD). The flux through the face ABCD is therefore:
\[ \rho v_1 [x_1-\Delta x_1/2, x_2, x_3] \Delta x_2 \Delta x_3. \]
Similarly, the flux through the face EFGH is: 
\[ \rho v_1 [x_1+\Delta x_1/2, x_2, x_3]. \]
The net flux = flux out of EFGH – flux into ABCD
\[ = \rho v_1 [x_1+\Delta x_1/2, x_2, x_3] - v_1 [x_1-\Delta x_1/2, x_2, x_3] \Delta x_2 \Delta x_3 \]
Similiarly for the other two directions. So the total flux into the volume element per unit volume = \( \rho \sum \partial v_1/\partial x_1 \) and since this is zero for an incompressible fluid, it follows that: 
\[ \sum \partial v_1/\partial x_1 = 0 \] (since \( \rho \neq 0 \). This is eqn (4.2.2). Eqn (4.2.3) follows if there is some accumulation in the volume element.

Exercise 4.3.1 Derive the formula (4.3.2) for the area of the orthogonal faces of the block shown in Fig. 4.3.1 using the following information. By the definition of the cross product, \( \Delta A \hat{n} = \frac{1}{2}(BC \times BD) \) where \( \Delta A \) is the area of the sloping face and BC and BD are vectors along the edges of that face. Show that BC = \( l_2 \hat{e}_3 - l_3 \hat{e}_2 \) and BD = \( l_1 \hat{e}_1 - l_2 \hat{e}_2 \). Calculate BC \( \times \) BD and use the result to verify eqn (4.3.2).

Solution
\[ \Delta A \hat{n} = \frac{1}{2}(BC \times BD). \]
\[ BC = BA + AC = (-l_2 \hat{e}_2 + l_3 \hat{e}_3); \quad BD = BA + AD = -l_2 \hat{e}_2 + l_1 \hat{e}_1 \]
\[ BC \times BD = (l_3 \hat{e}_3 - l_2 \hat{e}_2)(l_1 \hat{e}_1 - l_2 \hat{e}_2) \]

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\[
\begin{bmatrix}
0 \\
l_1 \\
l_2 \\
l_3
\end{bmatrix} \times
\begin{bmatrix}
l_1 \\
l_2 \\
l_3 \\
0
\end{bmatrix}
\]

The cross product is obtained from eqn A3.12 of Appendix A3:

\[
\Delta A \hat{n} = \frac{1}{2}
\begin{bmatrix}
e_1 & e_2 & e_3 \\
0 & -l_2 & l_3 \\
l_1 & -l_2 & 0
\end{bmatrix}
= \frac{1}{2}(l_4 l_1 e_1 + l_4 l_2 e_2 + l_4 l_3 e_3)
\]

Then \(\Delta A \hat{n} \cdot e_1 = \frac{1}{2}l_4 l_3 = \Delta A_1; \Delta A \hat{n} \cdot e_2 = \frac{1}{2}l_4 l_2 = \Delta A_2 \) and \(\Delta A \hat{n} \cdot e_3 = \frac{1}{2}l_4 l_1 = \Delta A_3\).

**Exercise. 4.4.1.** Establish eqn (4.4.4)

**Solution** Using eqn (A3.12) for the cross product in Eqn (4.4.4):

\[
\frac{2\pi}{l} (e_3 \times x) = \frac{2\pi}{l} \begin{bmatrix} e_1 & e_2 & e_3 \end{bmatrix} = \nu = \frac{2\pi}{l} [x_2 \hat{e}_1 + x_1 \hat{e}_2] \quad \text{or} \quad \nu = \begin{bmatrix} \frac{2\pi x_2}{l}, \frac{2\pi x_1}{l}, 0 \end{bmatrix}
\]

**Exercise 4.5.1** By writing out the components of the expression (4.5.10) for the local velocity field explicitly, and comparing the result with the first two terms of eqn (4.5.9), show that the components of the angular velocity \(\Omega\) are of the form \(\frac{1}{2}(\partial \nu_y/\partial x_j - \partial \nu_j/\partial x_i)\).

**Solution** Again using equation A3.12 for the cross product:

\[
\Omega(x) \times \Delta x = \begin{bmatrix} \hat{e}_1 & \hat{e}_2 & \hat{e}_3 \end{bmatrix}
\begin{bmatrix}
\Omega_1(x) & \Omega_2(x) & \Omega_3(x) \\
\Delta x_1 & \Delta x_2 & \Delta x_3
\end{bmatrix}
= [\Omega_1(x) \Delta x_2 - \Omega_2(x) \Delta x_1] \hat{e}_1 + \ldots
\]

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Thus the first component of \( \mathbf{v}(x) + \Omega(x)x \Delta x \) is \( v_1(x) + \Omega_2(x) \Delta x_1 - \Omega_3(x) \Delta x_2 \) \( \quad \) (1)

Compare this with the first component of eqn (4.5.9):

\[
v_1(x) + \frac{1}{2} \sum \left[ \frac{\partial v_1}{\partial x_j} \Delta x_j - \frac{\partial v_j}{\partial x_1} \Delta x_j \right] \Delta x_1 = \frac{1}{2} \left[ \frac{\partial v_1}{\partial x_2} - \frac{\partial v_2}{\partial x_1} \right] \Delta x_2 + \frac{1}{2} \left[ \frac{\partial v_1}{\partial x_3} - \frac{\partial v_3}{\partial x_1} \right] \Delta x_3 \]

Then comparing the coefficients of \( \Delta x_2 \) and \( \Delta x_3 \):

\[
\Omega_1(x) = \frac{1}{2} \left[ \frac{\partial v_2}{\partial x_1} - \frac{\partial v_1}{\partial x_2} \right] \quad \text{and} \quad \Omega_2(x) = \frac{1}{2} \left[ \frac{\partial v_1}{\partial x_3} - \frac{\partial v_3}{\partial x_1} \right]
\]

Similarly \( \Omega_3(x) = \frac{1}{2} \left[ \frac{\partial v_3}{\partial x_2} - \frac{\partial v_2}{\partial x_3} \right] \).

**Exercises.** 4.6.1 Establish eqn (4.6.4) using the fact that \( \Delta x_i = v_i \Delta t \) if \( \Delta t \) is small.

**Solution**

The expression \( (\partial \mathbf{v}/\partial t) \Delta t + \sum (\partial \mathbf{v}/\partial x_i) \Delta x_i \) assumes that the effects of each change of coordinate can be simply added together (linear additivity). The acceleration is obtained by dividing through by \( \Delta t \) and taking the limit as \( \Delta t \) tends to zero. That is:

\[
\lim_{\Delta t \to 0} \left[ \frac{\partial v}{\partial t} + \sum \frac{\partial v}{\partial x_i} \Delta x_i \right] \frac{\Delta t}{\Delta t} = \frac{\partial v}{\partial t} + \sum \frac{\partial v}{\partial x_i} v_i
\]

The last term is \( v_1 (\partial x^2_1) + v_2 (\partial x^2_2) + v_3 (\partial x^2_3) \) which is \( \mathbf{v} \cdot \nabla \mathbf{v} \) since, by definition (c.f. eqn (A3.14)) \( \nabla \mathbf{v} = [\partial v/\partial x_1, \partial v/\partial x_2, \partial v/\partial x_3] \).

**Exercises.** 4.7.1 Derive eqns (4.7.4) and (4.7.5). [Hint: Consider \( r(dv/dr)(dr) \).]

4.7.2 By solving eqn (4.7.5) show that the velocity field due to a rotating cylinder of radius \( R_1 \) in an infinite liquid is given by \( v = \Omega R^2 \) \( /r \) where \( \Omega \) is the angular velocity of the cylinder. Calculate the torque per unit length required to rotate the cylinder.

4.7.3 Derive an expression for the strain rate in the gap of a Couette viscometer in terms of the inner and outer radii, \( R_1 \) and \( R_2 \), and the angular velocity, \( \Omega \) of the outer cylinder.
Show that for very small gap widths, \(d\), this can be reduced to strain rate \(\dot{\gamma} = \Omega(R_1/d)\).

4.7.4 If the radius of the cylinders in a Couette viscometer is large compared to the gap width, \(d\), it is possible to approximate the flow in the gap by assuming it occurs between two parallel flat plates. The bottom plate, at \(R_1\), is stationary and the top plate, at \(R_2\), moves with velocity \(\Omega R_2\).

(a) Show that in that case the continuity equation gives \((\partial v_1/\partial x_1) = 0, v_2 = v_3 = 0\) and that the Navier-Stokes equation reduces to

\[
- \frac{\partial p}{\partial x_1} + \frac{d^2 v_1}{d x_2^2} = 0; \quad \frac{\partial p}{\partial x_2} = 0; \quad \frac{\partial p}{\partial x_3} = \rho g.
\]

(b) Hence show that \((d^2 v_1/d x_2^2) = 0\) and so \(v_1(x_2) = (\Omega R_2 x_2)/d\).

(c) Calculate the torque on the inner cylinder and verify that the result is in agreement with the general formula (eqn (4.7.5)) in this limit.

4.7.5 Show that if the cylinders in a Couette viscometer are filled to two different depths, \(L_1\) and \(L_2\) then even in the presence of ‘end effects’ we can still write:

\[\phi_2 - \phi_1 = K (L_2 - L_1) \eta \Omega\]

where \(\phi_1\) and \(\phi_2\) are the corresponding angles of twist of the torsion wire, and \(K\) is an instrument constant.

4.7.6 Assuming that the velocity \(v_1\) in eqn (4.7.9) depends only on the distance \(r\) from the centreline of the capillary tube, show that this equation reduces to the form (4.7.11). [Hint: first show that

\[
\frac{\partial^2 v}{\partial x_1^2} - \frac{d^2 v}{d r^2} \left( \frac{\partial}{\partial x_2} \right)^2 + \frac{d v}{d r} \frac{\partial^3 r}{\partial x_2^3} \right) \quad \text{and} \quad \partial r/\partial x_2 = x_2/r\]

4.7.7 Establish the results (4.7.12) and (4.7.13) for Poiseuille flow assuming that the pressures, \(p\), are purely hydrostatic.

4.7.8 A certain Ostwald viscometer has a capillary tube of length 5 cm and diameter 0.5 mm. Calculate the time required for the level of the water in the top reservoir to drop by 1 cm, assuming both reservoirs have a circular cross-section of diameter 1 cm. The temperature of the

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water is 20°C. You may assume that the term \((h_1 - h_2)/L \ll 1\) in eqn (4.7.13) for the flow rate.

4.7.9 Calculate the shear rate at the wall of the capillary tube for the viscometer described in the previous question.

4.7.10 In applying the hydrostatic formula (eqn (4.7.13)) for the pressure in the Ostwald viscometer, we have, in effect, neglected the \(\eta V^2\nu\) term in the equation of motion in the portion of the apparatus beyond the capillary tube. We aim to estimate the resulting error in the formula (4.7.13) for the flow rate. The order of magnitude of the neglected \(\eta V^2\nu\) term in this region is \(\eta V/(a'')^2\) where \(V\) and \(a''\) are the typical velocity and radius of the tube. These viscous forces must be balanced by an extra pressure gradient. With the aid of this estimate, show that the relative error in the final formula (4.7.13) for \(Q\) is of the order of \((a'')^4(L/\eta L)\) where \(L\) is the length of the viscometer tube beyond the capillary.

4.7.11 Hiemenz (1977) gives the following expression for the torque on the cone of a cone/plate viscometer

\[ M = \frac{4}{3} \pi R^3 \eta \Omega \cos \alpha \]

\[ \tan \alpha + \frac{1}{2} \{ \ln [(1 + \sin \alpha)/(1 - \sin \alpha)] \} \cos \alpha \]

Show that this reduces to eqn (4.7.15) for small \(\alpha\). (You will need the approximation \(\ln (1 + x) \approx x\) for small \(x\).)

4.7.12. Use the kind of argument displayed in Exercise (4.7.10) to show that for an Ostwald viscometer with a flow time of order 100 s, the inertial term (i.e. the L.H.S.) in the Navier-Stokes equation may safely be ignored.

4.7.13. Establish equation (4.7.11) using a force balance argument on a cylinder coaxial with the capillary tube (Fig. 4.7.2b).

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Solutions

4.7.1 From eqn (4.7.3):
\[ r^2 \frac{dv}{dr} - \frac{v}{r} = \frac{T_0}{2\pi \eta L} = K. \]

Now \[ r^2 \frac{d}{dr} (v/r) = r \left[ -\frac{v}{r^2} + \frac{1}{r} \frac{dv}{dr} \right] = \frac{dv}{dr} - \frac{v}{r} = \frac{K}{r^2} \]

\[ \therefore \frac{d}{dr} (v/r) = \frac{K}{r^3} \quad \text{and} \quad \int_{R_i}^{r} r^2 (v/r) \, dr = \int_{R_i}^{r} K \, dr \]

So \( v/r = K/2R_i^2 - K/2r^2 \) since \( v(R_i) = 0 \).

\[ i.e. \quad v = \frac{rT_o}{4\pi \eta L} \left[ \frac{1}{R_i^2} - \frac{1}{r^2} \right] \]

which is eqn (4.7.4).

Putting \( v = R_i \Omega \) when \( r = R_i \) gives \( T_o = 4\pi \eta L \Omega \left[ \frac{1}{R_i^2} - \frac{1}{R_o^2} \right] \)

from which eqn (4.7.5) follows immediately.

4.7.2 Integrating eqn (4.7.3) (see exercise 4.7.1) gives:

\[ \left[ \frac{v}{r} \right]_{R_i}^{r} = -\frac{1}{2} \left[ \frac{K}{r^2} \right]_{R_i}^{r}. \quad \text{If} \quad v = \Omega R_i \quad \text{at} \quad r = R_i \quad \text{then} \quad \frac{v}{r} = \Omega R_i / R_i = \frac{K}{2r_i^2} \left[ \frac{1}{R_i^2} - \frac{1}{r^2} \right] \]

Or \( v = \Omega r + \frac{K r^2}{2} \left[ \frac{1}{R_i^2} - \frac{1}{r^2} \right]. \quad \text{But} \quad v \to 0 \quad \text{as} \quad r \to \infty \quad \text{so that} \quad \Omega = -\frac{K}{2R_i^2}. \)

Then \( v = \Omega r - \frac{2R_i^2 \Omega}{r} \left[ \frac{1}{R_i^2} - \frac{1}{r^2} \right] = \frac{\Omega R_i^2}{r} \).

The torque per unit length required to rotate the cylinder is \( T_o / L = -2\pi \eta K \) (see exercise 4.7.1) \( = 2\pi \eta 2R_i^2 \Omega = 4\pi \eta R_i^2 \Omega \). (The negative sign indicates that this is the applied torque required to rotate the cylinder whereas \( T_o \) in exercise 4.7.1 is the torque delivered by the liquid to the bob.)

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4.7.3 The only non-zero elements of the rate of strain tensor are \( e_{12} \) and \( e_{21} \) and each is equal to \( \frac{1}{2}(dv/dr - v/r) \). The strain rate \( dv/dr = e_{21} + e_{12} = (dv/dr - v/r) \) as is suggested by equation (4.7.3). Note that it is not simply the velocity gradient \( dv/dr \) because one must subtract the rigid body aspect of the rotation. Since \( v = r \omega \), the strain rate can also be written \( r \delta \omega/dr \) where \( \omega(r) \) is the rate of rotation at various parts of the gap. (\( \omega(r) \) varies from zero on the inner cylinder to \( \Omega \) on the outer cylinder, or vice versa.) From eqn (4.7.4):

\[
\dot{\gamma} = \frac{dv}{dr} - \frac{v}{r} = \frac{T_o}{4\pi \eta L} \left[ \frac{1}{R_i^2} - \frac{1}{r^2} \right] + \frac{T_o}{4\pi \eta L} \frac{2}{r^3} - \frac{T_o}{4\pi \eta L} \left[ \frac{1}{R_i^2} - \frac{1}{r^2} \right]
\]

\[
\dot{\gamma} = \frac{T_o}{2\pi \eta L} r^2 \text{ and substituting for } T_o \text{ from equation (4.7.5)}:
\]

\[
\dot{\gamma} = \frac{R_i^2 R_o^2 \Omega}{(R_o^2 - R_i^2) r^2} \left( \frac{1}{R_i^2} - \frac{1}{R_o^2} \right)
\]

For a very small gap we have \( \dot{\gamma} = (2\Omega/r^2)[(R_o - R_i)(R_o + R_i)/R_o^2 + R_o^2 - r^2]^{-1} \) and putting \( r = R_i = R_o \) and \( R_o - R_i = d \) we can write \( \dot{\gamma} = (2\Omega/R_i^2)[d2R_i/R_i^4]^{-1} = \Omega R_i/d \).

4.7.4 We can assume that in this case there is no flow in the \( x_2 \) and \( x_3 \) direction (i.e. \( v_2 = v_3 = 0 \)) so that the continuity equation gives: \( \partial v_1/\partial x_1 + \partial v_2/\partial x_2 + \partial v_3/\partial x_3 = \partial v_1/\partial x_1 = 0 \). Then in the Navier-Stokes equation, neglecting the inertia terms: \( F = \Delta p + \eta \nabla^2 v = 0 \), the force \( F = \rho g \) is assumed to operate in the \( x_3 \) direction (whilst \( x \) measures the distance from the inner to the outer cylinder.) The components of the Navier-Stokes equation are therefore:

\[
0 - \frac{\partial p}{\partial x_1} + \eta \left[ \frac{\partial^2 v_1}{\partial x_1^2} + \frac{\partial^2 v_1}{\partial x_2^2} + \frac{\partial^2 v_1}{\partial x_3^2} \right] = 0 \quad (2)
\]

\[
0 - \frac{\partial p}{\partial x_2} = 0 \text{ because } v_2 = 0 \quad (3)
\]

and \( \rho g - \partial p/\partial x_3 = 0 \) because \( v_3 = 0 \). (4)
Equation (2) simplifies to:
\[- \partial p / \partial x_1 + \eta \partial^2 v_1 / \partial x_2^2 = 0 \quad (5)\]
because the other two terms are again zero and so \(v_1\) is a function of \(x_2\) only. Since \(v_1\) depends only on \(x_2\) and \(p\) is independent of \(x_2\) (from eqn (3)) it follows that the two terms in equation (5) must each be equal to a constant:
\[- \partial p / \partial x_1 = K = \eta \partial^2 v_1 / \partial x_2^2 \quad (6).\]

But \(\partial p / \partial x_1 = 0\) (since this corresponds to \(\partial p / \partial \theta\) for the cylinder and symmetry requires that the pressure be constant at all points on a circle around the axis of the viscometer.) Therefore \(\eta \partial^2 v_1 / \partial x_2^2 = 0\) and hence \(\partial v_1 / \partial x_2 = \text{a constant} = K'\). Then \(v_1 = K' x_2 + K''\) since \(v_1 = 0\) when \(x_2 = 0\), \(K'' = 0\) so \(v_1 = K' x_2\). But \(v_1 = \Omega R_2\) when \(x_2 = d\) so \(K' = \Omega R_2 / d\). Therefore \(v_1(x_2) = \Omega R_2 x_2 / d\). The shear rate in this case is \(\partial v_1 / \partial x_2 = K' = \Omega R_2 / d\). The torque on the inner cylinder (per unit area) is \(\Omega R_2 \eta R_2 / d\). From eqn (4.7.5) the torque per unit area on the inner cylinder is \(T_1 / 2 \pi R_i L = [2 R_2 R_o^2 / d (R_i + R_o)] \eta \Omega = \Omega \eta R_i R_o / d\) for \(R_i = R_o\).

4.7.5 The torque exerted on the inner cylinder, when filled to a depth \(I_1\) is (from eqn 4.7.5):
\[4 \pi L_1 R_1^2 R_o^2 \eta \Omega (R_o^2 - R_i^2) + T_1\] where \(T_1\) is the torque exerted on the inner cylinder by the motion of fluid in the bottom of the viscometer. \((T_1\) will be a function of \(\eta\) and \(\Omega\) but should not depend on \(I_1\) provided that the bob is lowered to the same point for each measurement.) When the viscometer is filled to depth \(I_2\), the torque is \[4 \pi L_2 R_2^2 R_o^2 \eta \Omega (R_o^2 - R_i^2) + T_2\] and the difference is \(K = \phi_2 - \phi_1 = K (I_2 - I_1) \eta \Omega\) where \(K'' = 4 \pi R_i^2 R_o^2 (R_o^2 - R_i^2)\). The change in the angles of twist of the torsion wire will be proportional to this change, so that \(\phi_2 - \phi_1 = K (I_2 - I_1) \eta \Omega\).

4.7.6 \(v = v(r)\) and \(r^2 = x_2^2 + x_3^2\); \(\partial v / \partial x_2 = (dv / dr) (\partial \theta / \partial x_2)\) and \(\partial v / \partial x_3 = (dv / dr) (\partial \theta / \partial x_3)\).

\[\frac{\partial^2 v}{\partial x_2^2} = \frac{\partial}{\partial x_2} \left( \frac{dv}{dr} \right) \frac{\partial r}{\partial x_2} + \frac{dv}{dr} \frac{\partial^2 r}{\partial x_2^2} = \frac{dv}{dr} \left( \frac{\partial r}{\partial x_2} \right)^2 + \frac{dv}{dr} \frac{\partial^2 r}{\partial x_2^2}.\]
But since $r^2 = x_2^2 + x_3^2$, $2rdr = 2x_2dx_2 + 2x_3dx_3$; \quad dr = x_2dx_2/r + x_3dx_3/r.$

Also $dr = \left[\partial r/\partial x_2\right]dx_2 + \left[\partial r/\partial x_3\right]dx_3$ so $\partial r/\partial x_2 = x_2/r$ and $\partial r/\partial x_3 = x_3/r$. Hence

$$\frac{\partial^2 \nu}{\partial x_2^2} + \frac{\partial^2 \nu}{\partial x_3^2} = \frac{d^2\nu}{dr^2}\left[\frac{\partial r}{\partial x_2}\right]^2 + \frac{d\nu}{dr}\left[\frac{\partial^2 r}{\partial x_2^2}\right] + \frac{d\nu}{dr}\left[\frac{\partial^2 r}{\partial x_3^2}\right] + \frac{d\nu}{dr}\left[\frac{\partial^2 r}{\partial x_2 \partial x_3}\right] (A)$$

$$\frac{\partial^2 \nu}{\partial x_2^2} = \frac{1}{r} - \frac{x_2^2}{r^2} \frac{\partial \nu}{\partial x_2} = \frac{1}{r} - \frac{x_2^2}{r^2} = \frac{1}{r^2} - \frac{x_2^2}{r^3} = \frac{x_2^2}{r^3}$$

Similarly $\frac{\partial^2 \nu}{\partial x_3^2} = \frac{x_3^2}{r^3}$ Substituting in eqn. (A):

$$\frac{d^2\nu}{dr^2}\left[\frac{x_2^2}{r^2} + \frac{x_3^2}{r^2}\right] + \frac{d\nu}{dr}\left[\frac{x_2^2}{r^2} + \frac{x_3^2}{r^2}\right]$$

i.e. $\partial^2 \nu/\partial x_2^2 + \partial^2 \nu/\partial x_3^2 = d^2\nu/dr^2 + (1/r)\frac{d\nu}{dr} - (1/r^2)\frac{d^2\nu}{dr^2}.$

Equation (4.7.11) follows immediately with $\nu = v_1$.

4.7.7

$$\frac{1}{r^2} \int \frac{d
u}{dr} = \frac{G}{\eta} \quad \text{so} \quad \int \frac{d
u}{dr} = \int \frac{G}{\eta}dr \quad \text{and so} \quad \frac{d
u}{dr} = \frac{Gr}{2\eta} + C$$

and $d\nu/dr = 0$ when $r = 0$ (on the tube axis) so $C = 0$. Then $\int d\nu = \int (G/2\eta)rdr$ and $v_1 = Gr^2/4\eta + C'$. But $v_1 = 0$ when $r = a$ so $C' = -Gr^2/4\eta$. \quad $\therefore v_1 = -G(a^2 - r^2)/4\eta$. (Eqn 4.7.12).
\[ Q = \int_0^a 2\pi r \nu \, dr = \int_0^a 2\pi \frac{G}{4\eta} (a^2 - r^2) \, dr \]

\[ = \frac{\pi G}{2\eta} \left[ \frac{a^2 r^2}{2} + \frac{r^4}{4} \right]_0^a = -\frac{\pi G a^4}{8\eta} \]

4.7.8 When water drops by 1 cm the volume of liquid flowing through the capillary is \( \pi \times \frac{1}{2} \times 1 \text{cm}^3 = 0.7854 \text{ cm}^3 \). 
\[ \frac{Q}{\pi \rho gd} = \frac{\pi \times 1 \times 981 \times (0.025)}{(8 \times 1.002 \times 10^2)} = 1.502 \times 10^{-2} \text{ cm}^3 \text{ s}^{-1} \]. (\( \eta \) is taken from Table 4.2 (= 1.002 mPa s = 1.002 \times 10^{-2} \text{ poise} ).
Time required = 0.7854/1.502\times10^{-2} = 52.3 \text{ sec}. 

4.7.9 Shear rate at the wall = \( [dv/dr]_{r=a} \) and, from eqn(4.7.12), \( \frac{dv}{dr}_{r=a} = G a^2 / \eta = 4 Q / \pi a^3 = 4 \times 1.502 \times 10^{-2} / [4 \times \pi \times (0.025)^3] = 1224 \text{ s}^{-1} \). (Wall shear rates of order 1000-2000 \text{ s}^{-1} are common in capillary viscometers.)

4.7.10 We need to compare the term \( \eta \nabla^2 \nu \) with the pressure gradient \( (p_1 - p_2) / L' \) in the reservoir. Note that \( V = Q / \pi a^2 \) so that \( \eta \nabla^2 \nu = \eta Q / \pi (a \gamma)^4 \).

\[ \frac{\eta \nabla^2 \nu}{\Delta p_t} = \frac{\eta Q}{\pi a^4} \frac{L'}{(p_1 - p_2)} = \frac{\eta Q}{\pi a^4} \frac{L'}{\rho g (h_1 + L - h_2)} \]

But \[ \frac{\eta Q}{\pi \rho g} = \frac{a^4 (h_1 + L - h_2)}{8L}, \] from eqn(4.7.13).

Hence \( \eta \nabla^2 \nu / \Delta p_t = [a / \gamma]^4 (L / L) \) as required. (The factor 8 makes the assumption \( \eta \nabla^2 \nu \ll \Delta p_t \) even more reasonable.

4.7.11

\[ M = \frac{4}{3} \frac{\pi R^3 \eta \Omega \cos \alpha}{\tan \alpha + \frac{1}{2} \ln \left( \frac{1 + \sin \alpha}{1 - \sin \alpha} \right) \cos \alpha} = \frac{4}{3} \frac{\pi R^3 \eta \Omega \cos \alpha}{\tan \alpha + \frac{1}{2} \ln \left( \frac{1 + \frac{2\sin \alpha}{1 - \sin \alpha}}{\cos \alpha} \right)} \]

S4.10
But $2 \sin \alpha/(1 + \sin \alpha)$ is small for small $\alpha$ and the $\ln$ function can be expanded to give:

$$M = \frac{4\pi R^3 \eta \Omega \cos \alpha}{\tan \alpha + \frac{1}{2}, \frac{2 \sin \alpha \cos \alpha}{1 - \sin \alpha}} = \frac{4\pi R^3 \eta \Omega \cos \alpha}{\tan \alpha + \frac{1}{2} \sin 2\alpha}.$$ 

For small $\alpha$ we have $\cos \alpha = 1$, $\tan \alpha = \alpha$ and $\frac{1}{2} \sin 2\alpha = \alpha$, so $M = (\alpha/3) \pi R^3 \eta (\Omega/\alpha)$.

4.7.12 We need to show that $\rho(\partial v/\partial t + v \cdot \nabla v)$ in the capillary is small compared to the term $\eta \nabla^2 v$. We note first that in the capillary, $v_2 = v_3 = 0$ and $\partial v_1/\partial x_1 = 0$. The term $v \cdot \nabla v$ is

$$\begin{align*}
\begin{pmatrix}
\frac{\partial v_1}{\partial x_1} + v_2 \frac{\partial v_1}{\partial x_2} + v_3 \frac{\partial v_1}{\partial x_3} \\
\frac{\partial v_2}{\partial x_1} + v_2 \frac{\partial v_2}{\partial x_2} + v_3 \frac{\partial v_2}{\partial x_3} \\
\frac{\partial v_3}{\partial x_1} + v_2 \frac{\partial v_3}{\partial x_2} + v_3 \frac{\partial v_3}{\partial x_3}
\end{pmatrix} = 0
\end{align*}$$

The other part of the inertial term $\rho \partial v/\partial t = \rho V/t_0$, where $V$ is the axial velocity and $t_0$ is the outflow time. Comparing this to the viscous term $(\eta \nabla^2 v = \eta V/a^2)$ the ratio is $(\rho V/t_0)/(\eta V/a^2) = \rho a^2 \eta t_0$. The normal values of $\rho = 10^3$ kg m$^{-3}$, $a = 10^{-3}$ m; $\eta = 10^{-3}$ N m$^{-2}$s and $t_0 = 100$ s would give this ratio $10^3 \times 10^{-3} / (10^{-3} \times 10^2) = 0.01$.

4.7.13 Driving force for the flow is the difference in the hydrostatic pressure $\Delta p$, between the top and bottom of the capillary which results in a force $\Delta p \times \text{area} = (\rho_1 - \rho_2)2\pi r d\Delta r$. The viscous force on the inside surface due to the adjoining fluid (which is moving faster) also pulls downwards with a force: $\eta \times \text{area} \times \text{shear rate} = 2\pi r \frac{d}{dr} (\rho v) \Delta r$. Also assisting the flow is the mass of liquid in the cylinder: $2\pi r p g L \Delta r$. Opposing the flow is the viscous drag on the outside wall:

$$\eta(2\pi r/dv/dr) \Delta r \Delta \Delta r.$$ 

Therefore $\Delta p = 2\pi r d\Delta r + 2\pi r p g L\Delta r$.
\[ \frac{d}{dr} \left( \frac{r \, dv}{dr} \right) = \frac{Gr}{\eta}. \] So \( \frac{dv}{dr} = \frac{Gr^2}{2\eta} \) or \( \frac{dv}{dr} = \frac{Gr}{2\eta} \)

\[ v = \int \frac{Gr}{2\eta} \, dr = \frac{Gr^2}{4\eta} + \text{const}. \]

But \( v = 0 \) when \( r = a \) so the constant is \(-Gr^2/4\eta\). Therefore \( v = -Gr(a^2 - r^2)/4\eta \).
Exercises. 4.8.1 Let $v_1$, $p_1$, and $v_2$, $p_2$ be two solutions to the continuity equation and eqn (4.8.2). Verify that the sum $v_1 + v_2$, $p_1 + p_2$ also satisfies the equations. (This is a consequence of the linearity of the equations). Show that this result is not true if eqn (4.8.2) is replaced by the full Navier-Stokes equation.

4.8.2 Satisfy yourself that the disturbance velocity $v + V = v + V \left( \cos \theta \hat{r} - \sin \theta \hat{\theta} \right)$ where $\hat{r}$ and $\hat{\theta}$ are unit orthogonal vectors with $\hat{r}$ directed radially from the particle centre. Hence show that, for large distances:

$$v + V = \left( 3a/2 \right) \left[ V + \left( V/2 \right) \sin \theta \hat{\theta} \right] \left( 1/r \right)$$

Solutions

4.8.1 $\nabla \cdot v = 0$ and $\rho \partial v / \partial t = F - \Delta p + \eta \nabla^2 v$. If $p_b$, $v_1$, and $p_b$, $v_2$ are solutions to these equations then $\nabla \cdot v_1 = 0$; $\nabla \cdot v_2 = 0$ and $\nabla \cdot (v_1 + v_2) = 0$. Also:

$$\rho \frac{\partial (v_1 + v_2)}{\partial t} = \rho \frac{\partial v_1}{\partial t} + \rho \frac{\partial v_2}{\partial t}$$

and these remain equal to one another. On the other hand the $v \nabla v$ form produces:

$$(v_1 + v_2) \nabla (v_1 + v_2)$$

which involved terms like $v \nabla v$ and $v \nabla v$ which cannot be eliminated.

4.8.2 From eqn (4.8.4):

$$v = \left[ -1 + \frac{3a}{2r} - \frac{a^3}{r^3} \right] V \cos \theta \hat{r} + \left[ 1 - \frac{3a}{4r} - \frac{a^3}{4r^3} \right] V \sin \theta \hat{\theta}.$$ 

$$v + V = v + V \cos \theta \hat{r} - V \sin \theta \hat{\theta}$$

$$= \left[ \frac{3a}{2r} - \frac{a^3}{2r^3} \right] V \cos \theta \hat{r} - \left[ \frac{3a}{4r} + \frac{a^3}{4r^3} \right] V \sin \theta \hat{\theta}.$$
(The disturbance velocity \( v + V \) is the velocity of the fluid relative to the laboratory reference frame. It varies from a value of \( V \) at all points on the surface of the particle (which are moving with the particle) to zero at distances far from the particle (where the fluid is unaffected). Component of \( V \) along vector \( r \) is \( V \cos \theta \) and the component along the \( \theta \) vector is \( -V \sin \theta \). (See figure.)

\[
\begin{align*}
\nu + V &= \frac{2a}{2r} V \cos \theta \hat{r} - \frac{3a}{4r} V \sin \theta \hat{\theta} \\
&= \frac{3}{2} a \left( V \cos \theta \hat{r} - \frac{1}{2} V \sin \theta \hat{\theta} \right) \frac{1}{r}
\end{align*}
\]

For large distances

\[
= \frac{3}{2} a \left( V - \frac{1}{2} V \sin \theta \right) \frac{1}{r} \quad \text{using} \quad V = V \cos \theta \hat{r} - \sin \theta \hat{\theta}.
\]

**Exercises.**

4.9.1 Establish eqn (4.9.13).

4.9.2 By using a suitable approximation for small values of \( \theta \) in eqn (4.9.16), derive eqn (4.9.14) for the mean squared orientation change of a particle during a small period \( t \).

4.9.3 Calculate the value of \( D_r \) for values of \( a/b \) from 1 to 20 and \( a = 10^{-7} \) m using eqn (4.9.18). Show that for large \( a/b \), this formula takes the approximate form

\[
D_r = \frac{3kT}{32\pi \eta a^3} \left[ 2 \ln \left( \frac{2a}{b} \right) - 1 \right]
\]

Compare values obtained with this formula with the exact value obtained earlier.

4.9.4 Alexander and Johnson (1949; p. 400) quote a value of \( D_r = 7 \) s\(^{-1} \) obtained by Edsall for the rotary diffusion constant of rabbit myosin at \( T = 276 \) K. Taking the viscosity of water as \( 1.6 \times 10^{-3} \) Pa s at this temperature and a high value (say \( a/b = 100 \)) for the axial ratio, estimate the length of the myosin molecule. (Independent measurements of the particle volume would permit a further refinement of this result.)

S4.14
4.9.5 For an oblate (disc-shaped) particle the rotational diffusivity $D_r$, is given by

$$D_r = \frac{kT}{16\pi\eta ab^2(1 - q^2)} \left[ 3q^2(2 - q^2)(q^2 - 1)^2 \arctan(q^2 - 1)^2 + 3 \right]$$

Show that for $q \gg 1$ (i.e. a flat disc): $D_r = 3kT/32\pi b^3$.

---

**Solutions 4.9.1**

$$m \frac{d\langle V \rangle}{dt} = -6\pi\eta a\langle V \rangle \quad \text{so} \quad \frac{d\langle V \rangle}{\langle V \rangle} = \frac{d\ln\langle V \rangle}{m} = \frac{-6\pi\eta a}{m} dt$$

Integrating $\langle V \rangle = \langle V_0 \rangle \exp(-\gamma/\tau_p)$ where $\tau_p = 6\pi\eta a/m$.

4.9.2 $\langle \cos \theta \rangle = \exp(-2D_f)$ and $\cos \theta = 1 - \theta^2/2$. $\langle 1 - \theta^2/2 \rangle = 1 - 2D_f$ for small $\theta$. (The exponential can be expanded because for small $\theta$, $\cos \theta \sim 1$ so the exponent must be very small and hence $\exp(-x) \sim 1 - x$.) It follows that $\langle \theta^2(t) \rangle = 4D_f$.

4.9.3 $a/b = q^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_r$</td>
<td>184</td>
<td>486</td>
<td>704</td>
<td>863</td>
<td>987</td>
<td>1088</td>
<td>1173</td>
<td>1247</td>
<td>1312</td>
<td>1370</td>
</tr>
<tr>
<td>$a/b$</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>$D_r$</td>
<td>1423</td>
<td>1471</td>
<td>1515</td>
<td>1555</td>
<td>1593</td>
<td>1629</td>
<td>1662</td>
<td>1693</td>
<td>1724</td>
<td>1752</td>
</tr>
</tbody>
</table>

$D_r = 1.38 \times 10^{21} \times 298 f(q) \pi a^3 q^2 = [1.38 \times 10^{-23} \times 298 / (10^{-21} \times 8\pi \times 8.9 \times 10^{-4})] f(q) q^2$. In units $J/(Pa s m^3) = s^{-1}$. $D_r = 183 f(q) \hat{q}$ where $f(q)$ is given in equation (4.9.18).

Using the approximation formula:

$$D_r = \frac{3 \times 1.38 \times 10^{-23} \times 298}{16\pi \times 8.9 \times 10^{-4} \times 10^{-21}} \left[ 2 \ln \left( \frac{2a}{b} \right) - 1 \right] = 275 [2 \ln (2a/b) - 1]$$

<table>
<thead>
<tr>
<th></th>
<th>20</th>
<th>18</th>
<th>16</th>
<th>14</th>
<th>12</th>
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<th>6</th>
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<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_r$</td>
<td>1756</td>
<td>1698</td>
<td>1633</td>
<td>1560</td>
<td>1474</td>
<td>1374</td>
<td>1252</td>
<td>1178</td>
<td>1093</td>
<td>992</td>
<td>870</td>
</tr>
<tr>
<td>$a/b$</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_r$</td>
<td>711</td>
<td>488</td>
<td>-</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Evidently the simple formula can be used for any value of $a/b$ greater than 2, with an
error of < 1%. For large $a/b$ (i.e. small $q$) we have:

$$D_t = \frac{kT}{8\pi \eta b} \left[ 3q^2 \times 2 \times \ln(2q^{-1}) - 3q^2 \right]/2 = \frac{3kT}{16\pi \eta a^3} \left[ 2 \ln \left( \frac{2a}{b} \right) - 1 \right]$$

For values of $a/b$ between 1 and 2:

<table>
<thead>
<tr>
<th>$a/b$</th>
<th>2</th>
<th>1.8</th>
<th>1.6</th>
<th>1.5</th>
<th>1.4</th>
<th>1.2</th>
<th>1.1</th>
<th>1.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_t$ (approx.)</td>
<td>487</td>
<td>433</td>
<td>375</td>
<td>345</td>
<td>314</td>
<td>249</td>
<td>216</td>
<td>200</td>
</tr>
<tr>
<td>$D_t$ (approx.)</td>
<td>487</td>
<td>430</td>
<td>365</td>
<td>329</td>
<td>292</td>
<td>207</td>
<td>158</td>
<td>134</td>
</tr>
</tbody>
</table>

At $a/b = 1.5$ the error is ~ 3%, rising to 20% at 1.2.

4.9.4 For $a/b = 100$, $D_t = 1.358 \times 10^{-18} a^3$ s so that $a = 5.79 \times 10^{-7} \text{ m} = 579 \text{ nm}$.

For $a/b = 50$, $D_t = 1.162 \times 10^{-18} a^3$ s and $a = 550 \text{ nm}$.

For $a/b = 20$, $D_t = 9.02 \times 10^{-19} a^3$ s and $a = 505 \text{ nm}$.

So as long as $a/b$ is large we find $a = 500 - 580 \text{ nm}$.

4.9.5

$$D_t = \frac{kT}{8\pi \eta b} \left[ \frac{3q^2(-q^2)}{q} \arctan q \right](-2q^4) = \frac{kTq}{8\pi \eta b^3} \left[ \frac{-3q^3}{2} \right] \frac{1}{-2q^4} = \frac{3kT}{32\eta b^3}$$

---

**Exercises**

4.10.1 In deriving the formula (4.10.4) for the macroscopic stress tensor in a suspension of rigid particles, we used the fact that $e = 0$ inside the particles. Establish this result by calculating the strain tensor for the rigid body velocity field $V + \Omega \times x$.

4.10.2 Establish eqn (4.10.14) using the suggested integration procedure.

4.10.3 Show that $S_{ij}$ in eqn (4.10.15) is proportional to $D\eta/\omega^2$ where $D$ is the particle diffusion coefficient.

4.10.4 Calculate $S_i$ for the suspensions shown in Fig. 4.10.5 assuming the particle radius is 100nm and temperature is 25°C. At what shear rate is the suspension viscosity half way between $\eta_1^*$ and $\eta_2^*$? What do $\eta_1^*$ and $\eta_2^*$ represent?

---

**Solutions**

4.10.1 $V + \Omega \times x = q$ (say). Now $e = (1/2\eta) \sigma^D$ and $e_y = (1/2\eta) \sigma_{yy}^D$ (eqn. 4.5.5)

S4.16
So \( e = \frac{1}{2} \left[ \frac{\partial q_i}{\partial x_j} + \frac{\partial q_j}{\partial x_i} \right] = \frac{1}{2} \left[ \frac{\partial V_i}{\partial x_j} + \frac{\partial (\Omega \times x)_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i} + \frac{\partial (\Omega \times x)_j}{\partial x_i} \right] \)

But \( \Omega \times x = \begin{bmatrix} \Omega_1 & \Omega_2 & \Omega_3 \\ x_1 & x_2 & x_3 \end{bmatrix} = (\Omega_1 x_1 - \Omega_2 x_2)e_1 + (\Omega_2 x_3 - \Omega_1 x_3)e_2 \\
+ (\Omega_3 x_2 - \Omega_1 x_1)e_3 \)

\[ = \sum (\Omega_i x_i - \Omega_j x_j)e_i. \]

\[ e_{12} = \frac{1}{2} \left[ \frac{\partial V_1}{\partial x_2} + \frac{\partial V_2}{\partial x_1} + \frac{\partial (\Omega_1 x_2 - \Omega_2 x_1)}{\partial x_2} + \frac{\partial (\Omega_2 x_1 - \Omega_1 x_2)}{\partial x_1} \right] \]

\( e_{12} = -\Omega_3 + \Omega_3 = 0 \) since \( V \) is constant. The same result can be established for each of the terms in \( e \).

4.10.2 \( d\eta^* = -2.5 \eta^* d\phi/(1 - K\phi) = 2.5 \eta^* d\phi/(1 - \phi/p). \) So \( d\eta^*/\eta^* = -2.5 p \phi/(1 - \phi/p) \)

\( \ln \eta^*/\eta = -2.5 p \left[ \ln(1 - \phi/p) \right] \ln \eta^*/\eta = \eta^* \left[ 1 - \phi/p \right]^{-2.5p}. \)

4.10.3 \( S_i = kT/\alpha a^3 \) and \( D = kT/B - kT/6\pi\eta a. \) Therefore \( S_i = D/6\pi\eta a/\alpha a^3 = 6\pi\eta D/\alpha a^2. \)

4.10.4 \( S_i = kT/0.431 \times (10^{-7})^3 = 1.38 \times 10^{-23} \times 298/(0.431 \times (10^{-7})^3) = 9.54 \text{ N m}^2. \)

When \( S = S_i = 9.54 \text{ N m}^2 \) we have (from equation 4.10.15): \( (\eta^* - \eta_1^*)(\eta_2^* - \eta_1^*) = \)

\( \frac{1}{2} \) so \( \eta^* = \eta_1^* + \frac{1}{2}(\eta_2^* - \eta_1^*) = (\eta_1^* + \eta_2^*)/2 \) so this is the required shear rate. It corresponds to \( S = kT/\alpha a^3 \).

\[ \lim_{s \to \infty} \frac{\eta^* - \eta_1^*}{\eta_2^* - \eta_1^*} = 1 \] \( \text{i.e.} \eta^* = \eta_2^*. \)

\[ \lim_{s \to \infty} \frac{\eta_2^* - \eta_1^*}{\eta_2^* - \eta_1^*} = 0 \] \( \text{i.e.} \eta_2^* \) is the low shear limiting viscosity and \( \eta_1^* \) is the high shear limiting value.

S4.17

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Chapter 5
Solutions

Exercises. 5.2.1 Show that the average radius \( \bar{r} \) of spherical particles is given by:

\[
\bar{r} = \left( \frac{3cV}{4\pi\rho N} \right)^{1/3}
\]

where \( \rho \) is the particle density, \( c \) is the concentration of the sol (by mass) and it is found to contain \( N \) particles in a volume \( V \).

5.2.2. The wavelength associated with an electron is given by the de Broglie relation, \( \lambda = h/p = h/(2m_eE)^{1/2} \), where \( h \) is Planck’s constant, \( p \) is the electron momentum, \( m_e \) its mass and \( E \) its kinetic energy. Estimate the wavelength of an electron that has been accelerated through a voltage of 10kV so that it has acquired an energy, \( E \), of 10keV. [A typical acceleration voltage would be of this order.]

Solutions

5.2.1 If \( V_{av} \) ~ average volume per particle, then

\[
V_{av} = \frac{4}{3} \pi \bar{r}^3 \quad \text{and} \quad NV_{av} = \frac{Vc}{\rho}
\]

where \( V = \) volume of the solution, \( c = \) mass per unit volume of solution and \( \rho \) is the density of the solid. Therefore \( \bar{r} = \left[ \frac{3}{cV/4\pi\rho N} \right]^{1/3} \).

5.2.2 \( \lambda = (6.626 \times 10^{-34}) (2 \times 9.1096 \times 10^{-31} \times 1.602 \times 10^{-19}) \) (for an energy of 10 keV = 10^4 \times \text{1.602} \times 10^{-19}J.) \( \lambda = 1.23 \times 10^{-12} \text{ m} = 0.012 \text{ nm} \). This is obviously not the factor which limits resolution of the electron microscope. Rather it is the distortion which occurs in the magnetic and electrostatic focussing devices.

Exercises. 5.3.1 Calculate the mean, standard deviation, and the variance of the distribution shown in Table 5.1. What is the difference between the mean and the mode in this case?

5.3.2 Establish eqn (5.3.3) from (5.3.2).

5.3.3 Calculate the number area mean diameter, \( \bar{d}_{na} \), of the particles described in Table 5.1 and compare it with the number length mean diameter. Show that \( \bar{d}_{na} = (\sigma^2 + \bar{d}^2)^{1/2} \), and check this with the result obtained in Exercise 5.3.1 (note the relevance to eqn (5.3.13)).

S5.1
5.3.4 The accompanying figure (5.3.4) shows a simple distribution function which can be approximated by a parabola:

\[ F(d_i) = a + b \frac{d_i}{d} + c \left( \frac{d_i}{d} \right)^2. \]

Show that \[ F = \frac{3N d_i}{2d^2} \left( 1 - \frac{d_i}{2d} \right) \]

where \( N \) is the number of particles. [Hint: First show that \( F = bn(1 - u/2) \) where \( u = d_i/d \). ]

**FIGURE 5.3.4**

Verify that \( \bar{d} = \int d_i \, dn_i / \int dn_i \). What is the maximum value of \( F \)?

5.3.5 Calculate the number (arithmetic) mean of \( d_i / \bar{d} \) or \( J_{\text{nl}} \) and its standard deviation and do the same for \( \ln d_i \) for the distribution in Table 5.3. What is the (number length) geometric mean diameter of these particles?

5.3.6 Calculate the number volume mean diameter of the particles in Table 5.1 and compare it with the number area mean diameter calculated in Exercise 5.3.3. Why is it larger? Is this always true?

Show that the mass average diameter, \( \bar{d}_{\text{mls}} \), is the ratio of the fourth to the third moment of the distribution.

**Solutions 5.3.1**

\( \bar{d} = 307.4 \text{ nm}; \sigma = 103 \text{ nm}; \sigma^2 = 10.6 \times 10^3 \text{ Mode} = 275 \text{ nm}; \text{ diff} = 32 \text{ nm} \)

5.3.2

\[ \sigma^2 = \sum f_i (d_i - \bar{d})^2 = \sum f_i (d_i^2 - 2d_i \bar{d} + \bar{d}^2) = \sum f_i d_i^2 - 2\bar{d} \sum f_i d_i + \bar{d}^2 \sum f_i = d_i^2 - 2\bar{d} + \bar{d}^2 = \bar{d}^2 - \bar{d}^2 = \bar{d}^2 \]

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5.3.3

\[ \bar{d} = 307.4 \text{ nm} \quad \text{and} \quad \bar{d}_{\text{NA}} = 324.2 \text{ nm}. \quad \text{\( \bar{d}_{\text{NA}} \) is always greater than \( \bar{d}_{\text{NL}} \).} \]

because the former favours larger particle sizes. \( \bar{d}_{\text{NA}} = \left( \bar{d}^2 \right)^{1/4} \) from eqn(5.3.3).

Substituting for \( \sigma^2 \) and \( \bar{d}^2 \) from exercise5.3.1 gives \( \bar{d}_{\text{NA}} = 324.2 \text{ nm} \).

5.3.4

\[ F(d_i) = a + b \frac{d_i}{\bar{d}} + \frac{c}{2} \left( \frac{d_i}{\bar{d}} \right)^2 \]
\[ \text{or} \quad F(u) = a + bu + cu^2 \quad \text{where} \quad u = d_i/\bar{d}. \]

At \( d_i = 0 \) and \( 2\bar{d} \), \( F(d_i) = 0 \).

Therefore, \( a = 0 \) and \( 2b + 4c = 0 \) or \( c = -b/2 \). i.e. \( F(u) = bu - \frac{1}{2}bu^2 \).

But \( N = \int dE_i = \int F(d_i)dd_i = \int \left( \frac{bu^2}{2} - \frac{b}{2} \frac{u^3}{3} \right) \left| _0^{2\bar{d}} \right. = 2b\bar{d}/3. \)

So \( b = 3N/2\bar{d} \) and \( c = -3N/4\bar{d} \). Then \( F = \frac{3N}{2} \frac{d_i}{\bar{d}} \left( 1 - \frac{d_i}{2\bar{d}} \right) \)

\[ \frac{dE_i}{dn_i} = \int \frac{d_iF(d_i/\bar{d})}{N} = \frac{3\bar{d}}{2} \left\{ \frac{d_i^2}{2\bar{d}} \left[ 1 - \frac{d_i}{2\bar{d}} \right] dd_i \right\} \]

\[ = \frac{3}{2\bar{d}} \left[ \frac{d_i^3}{3} - \frac{d_i^4}{8\bar{d}} \right] \left| _0^{2\bar{d}} \right. = \frac{3}{2\bar{d}} \left[ \frac{8\bar{d}^3}{3} - 2\bar{d}^3 \right] = \bar{d}. \]

The maximum value of \( F \) occurs when \( d_i = \bar{d} \) and is \( 3N/4\bar{d} \).

S5.3
5.3.5

$$d_{ml} = 546 \text{ nm}; \quad \sigma = 488 \text{ nm}; \quad \ln(d) = 6.006; \quad \sigma_g = 0.598; \quad d_g = 403 \text{ nm}.$$ 

5.3.6 $$d_{nv} = 339.5 \text{ nm}. \quad \text{It is always larger because } d_{nv} = \left(d_{nl}^{1/3}\right)^3 \text{ and}$$

$$d_{nl} = \left[d_{nl}^{1/3}\right]^6. \quad \text{The volume average will give greater weight}$$

$$\text{to larger particles. } d_{ml} = \sum m_i / \sum m_i. \quad \text{For spherical particles}$$

$$d_{ml} = \left[\frac{\sum \pi d_i^3 \rho d_i / 6}{\sum \pi d_i^3 / 6}\right] = \frac{\sum d_i^4}{\sum d_i^2}, \quad \text{where } \rho \text{ is the density.}$$

Exercises.

5.4.1 Show that the normal distribution curve has inflexions on either side of the mean and the distance between them is 2\(\sigma\).

5.4.2(i) Show that, for the distribution described in Exercise 5.3.4, the standard deviation is given by \(\sigma = d - d_{nl}\).

(ii) What fraction of the material lies between \(d \pm \sigma\) in this case? Compare this with the normal distribution.

Solutions

5.4.1

$$f_0(x) = \frac{1}{\sigma \sqrt{(2\pi)}} \exp\left[-\frac{1}{2} \frac{(x - \bar{x})^2}{\sigma^2}\right] \quad \text{so that } \quad f_0'(x) = \frac{- (x - \bar{x})}{\sigma \sqrt{(2\pi)}} \exp\left[-\frac{1}{2} \frac{(x - \bar{x})^2}{\sigma^2}\right]$$

$$f_0''(x) = \frac{(x - \bar{x})^2}{\sigma \sqrt{(2\pi)}} \exp\left[-\frac{1}{2} \frac{(x - \bar{x})^2}{\sigma^2}\right] - \frac{1}{\sigma \sqrt{(2\pi)}} \exp[\ldots]$$

$$= \frac{1}{\sigma \sqrt{(2\pi)}} \exp\left[-\frac{1}{2} \frac{(x - \bar{x})^2}{\sigma^2}\right] \left[\frac{(x - \bar{x})^2}{\sigma^2} - 1\right] = 0 \quad \text{when } x - \bar{x} = \pm \sigma.$$
Therefore, inflexions occur at distances of \( \pm \sigma \) from the mean value (i.e. \( 2\sigma \) apart).

5.4.2(i)

\[
\sigma = \sqrt{\frac{\int (d-\bar{d})^2 \, dn}{N}} = \sqrt{\frac{\sigma^2}{N} \int (d-\bar{d} - 1) \, dn} \\
= \sqrt{\frac{d}{N} \int_0^1 (u-1)^2 \frac{3N}{2} u(1-u/2) \, du} \\
= \frac{\sqrt{3}}{2} \sqrt{\frac{5u^3}{3} - \frac{5u^4}{3} + \frac{u^5}{5}} \bigg|_{0}^{1} = \frac{\bar{d}}{\sqrt{5}}
\]

5.4.2(ii)

\[
n = \frac{1}{\sqrt{5}} \int_{1/\sqrt{5}}^{1} F \, du = \int_{1/\sqrt{5}}^{1} \frac{3N}{2} u(1-u/2) \, du \\
= \frac{3N}{2} \left[ \frac{u^2}{2} - \frac{u^3}{6} \right]_{1/\sqrt{5}}^{1} = (7\sqrt{5} + 25)N = 0.626N.
\]

i.e. 62.6\% of the sample lies in this region compared to 68.2\% for the normal distribution.

**Exercises.** 5.5.1 The following table gives values of the mass, \( M \), of material deposited as a function of time on a balance pan suspended in a settling dispersion. Draw up a cumulative size distribution using the method described in connection with eqn (5.5.3). The pan has a radius of 2 cm and is exactly 15 cm below the surface of the (aqueous) suspension. The initial concentration of the suspension is 5.50 g L\(^{-1}\) and the density of the solid is 4.80 g cm\(^{-3}\). (Take the density of water as 1.00 g cm\(^{-3}\) and assume that \( \eta = 10^{-3} \) g cm\(^{-1}\) s\(^{-1}\).)

(Ignore convective effects and assume that the expected maximum deposition corresponds to the mass of the solid in the column of liquid above the pan.)
<table>
<thead>
<tr>
<th>$M$ (mg)</th>
<th>0</th>
<th>31</th>
<th>67</th>
<th>104</th>
<th>145</th>
<th>166</th>
<th>207</th>
<th>238</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$ (sec)</td>
<td>27</td>
<td>40</td>
<td>55</td>
<td>74</td>
<td>99</td>
<td>122</td>
<td>134</td>
<td>148</td>
</tr>
<tr>
<td>$M$ (mg)</td>
<td>290</td>
<td>311</td>
<td>363</td>
<td>415</td>
<td>487</td>
<td>518</td>
<td>549</td>
<td></td>
</tr>
<tr>
<td>$t$ (sec)</td>
<td>181</td>
<td>200</td>
<td>270</td>
<td>330</td>
<td>403</td>
<td>493</td>
<td>545</td>
<td></td>
</tr>
<tr>
<td>$M$ (mg)</td>
<td>591</td>
<td>632</td>
<td>653</td>
<td>684</td>
<td>705</td>
<td>726</td>
<td>746</td>
<td></td>
</tr>
<tr>
<td>$t$ (sec)</td>
<td>665</td>
<td>898</td>
<td>1097</td>
<td>1340</td>
<td>1810</td>
<td>2440</td>
<td>2980</td>
<td></td>
</tr>
</tbody>
</table>

5.5.2 When protein A is subjected to ultracentrifugation at 20°C, the particle boundary is found to move from a position 6.231 cm from the axis of the rotor at time $t = 0$ s to a distance of 6.823 cm after $t = 4500$ s. Calculate the sedimentation coefficient $S$ for protein A. Given that its diffusion coefficient is $2.2 \times 10^{-6}$ cm$^2$ s$^{-1}$ and its partial specific volume is $0.80$ g/cm$^3$, estimate its molar mass. ($\rho_1$ at 20°C for water = 0.9982 g cm$^{-3}$)

Solutions

5.5.1 Maximum possible deposition $= 15 \times \pi \times 2^2 \times 5.5 \times 10^{-3}$ g/cm$^3 = 1.037$ g

Plot $M$ against $t$ for $0 < t < 3000$ s. Draw tangents and estimate $m\%$ from the intercept and plot against $t$ (Fig. 3). Convert $t$ into a size and the resulting plot should look like the cumulative distribution curve for the particle size. (Fig 2)

![Figure 1](image1.png)

![Figure 2](image2.png)

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In the alternative procedure suggested by Fig 5.5.1(b), we plot \( M/M_{\text{tot}} \) against \( \ln t \). Then draw tangents to obtain \( dM/d\ln t \) and subtract this from the curve for \( M \) to give the curve for \( m \) (by difference) or use the values of \( dM/d\ln t \equiv t \, dM/dt \) as the measure of particles smaller than the cut off size. (Again the abscissa has to be converted from \( \ln t \) into the corresponding size using equation (5.5.4). Diameter corresponding to \( t \) sec sedimentation time is \( d = [(18 \times 10^{-3} \times 15)/(3.8 \times 981)]^{1/5} \, \text{cm} = 0.027/r^{1/5} \) (microns).

Converting the \( t \) into diameter gives the percent oversize for each diameter which is shown in figure 3. There is a clear maximum in the size distribution at \( d = 12 \, \mu m \) and a less well defined one at about \( d = 8 \, \mu m \).

The second method does not look so good with this data. Figure 4 shows that the estimated slopes are too high at the lowest values of \( t \). When \( m \) begins to show positive values (for \( \ln t > 5.2 \), there is a step in \( m \) at about \( \ln t = 6.5 \) (corresponding to the maximum at \( d = 12 \, \mu m \) as before) but there is considerable scatter in the slope values. Perhaps a smoothed polynomial function representing the original data could be more easily and effectively differentiated.

5.5.2 Substituting in equation (3.1.12): \( \ln(6.823/6.231) = S \times (30 \, 000 \times 2\pi/60)^2 \times 4500 \) gives \( S = 2.04 \times 10^{-12} \) s = 20.4 svedbergs. Substituting in equation (3.1.11) gives:

\[
M = (2.04 \times 10^{-12}\times 8.31 \times 293 \times 10^{7})(2.2 \times 10^{-6} \times (1 - 0.80 \times 0.9982)) \, \text{g mol}^{-1} = 112 \, 000.
\]
(Note the conversion of \( R \) from joules to ergs.)

**Exercises** 5.6.1 Establish equation 5.6.5 assuming that the particle and the fluid can be treated as a pair of parallel resistors in the region where the particle is located.

5.6.2 Compare the result obtained with eqns (5.6.7) and (5.6.8) for particles of diameter 1, 2, 4, 8, 16 and 32 \( \mu \text{m} \) measured with an orifice of diameter 100 \( \mu \text{m} \). (Replace the cylinder with \( d - l \) by a sphere of diameter \( d \)).

**Solutions** 5.6.1

\[
R_0 = \frac{\sigma_o \delta l}{A} \quad \text{and} \quad \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} = \frac{(A-a)}{\sigma_o \delta l} + \frac{a}{\sigma o \delta l} = \frac{\sigma(A-a)}{\sigma_o \delta l} + \frac{\sigma_o a}{\sigma_o \delta l}
\]

\[
R = \frac{\sigma_o \sigma \delta l}{\sigma A - a(\sigma - \sigma_o)} \quad \Rightarrow \quad \delta R = \frac{\sigma_o \sigma \delta l}{\sigma A - a(\sigma - \sigma_o)} - \frac{\sigma_o \delta l}{A}
\]

\[
\delta R = \sigma_o \delta l \left[ \frac{1}{A-a(1-\frac{u_o}{\sigma})} - \frac{1}{A} \right] = \sigma_o \delta l \left[ \frac{1}{A-pu} - \frac{1}{A} \right]
\]

\[
= \frac{\sigma_o \delta l}{A} \left[ \frac{pa}{A(A-pa)} \right] = \frac{a \sigma_o p \delta l}{A^2(1-pa/A)} \quad \text{which is eqn. (5.6.5)}.
\]

5.6.2 From eqn (5.6.7) if \( p - d/D \):

\[
\frac{\Delta R}{\sigma_o} = \frac{a l}{A} \left( \frac{1-\frac{a}{A}}{A} \right)^{-1} \quad \text{and} \quad \frac{a}{A} = p^2, \quad l/A = -\frac{p}{\pi D}
\]

\[
\Rightarrow \quad \frac{\pi \Delta R D}{\sigma_o} = p^2 p(1-p^2)^{-1} = p^3 \text{ for small } p.
\]

From eqn (5.6.8):

\[
\frac{\pi \Delta R D}{\sigma_o} = 4 \left[ \frac{\arcsin p}{(1-p^2)^{\frac{1}{2}}} - p \right] = 4p \left[ (1-p^2)^{-\frac{1}{2}} - 1 \right]
\]

\[
= 4p(1 + \frac{1}{2}p^2 - 1) \text{ for small } p = 2p^3.
\]
\[ d = \begin{array}{cccccc}
1 & 2 & 4 & 8 & 16 & 32 \\
n / D = & 0.01 & 0.02 & 0.04 & 0.08 & 0.16 & 0.32 \\
p^2 = & 10^{-4} & 4 \times 10^{-4} & 1.6 \times 10^{-3} & 6.4 \times 10^{-3} & 2.56 \times 10^{-2} & 0.1024 \\
\pi \Delta R/\phi_0 \\
\text{(eqn 5.6.7)} & 1 \times 10^{-6} & 8 \times 10^{-6} & 6.4 \times 10^{-5} & 5.15 \times 10^{-4} & 4.204 \times 10^{-3} & 0.03651 \\
\text{eqn (5.6.8)} & 2 \times 10^{-6} & 1.6 \times 10^{-5} & 1.28 \times 10^{-4} & 1.029 \times 10^{-3} & 8.535 \times 10^{-3} & 0.07104 \\
\end{array} \]

**Exercises**

5.7.1 Show that the final integral in equation (5.7.1) for \( P_x(\theta) = 1 \) is equal to 8/3.

5.7.2 Establish equation (5.7.4).

5.7.3 Derive eqn. (5.7.11) from (5.7.10).

5.7.4 Establish eqn (5.7.7) from (3.3.7). Kerker (1969) gives the following alternative forms (which you can verify): \( \mathcal{H}m' = H (p_1 + p_2) \) where \( m' \) is the mass fraction, \( \rho_1 \) is the density of the solution, \( \rho_2 \) is the density of the solid spheres. Since \( \phi = (\rho_1 + \rho_2) m' = c \rho_1 \), where \( c \) is the concentration (mass of solid per unit volume of solution), this can also be written \( \mathcal{H}c = H M N_A \Delta \rho_2 \) where \( M \) is the molar mass.

5.7.5 Verify the differential formula for \( K_f(Q) \) in eqn (5.7.17) and show that \( K_f(Q) = \lim (\tau \to 0) \) of \( [d^2 \ln g^{(1)}(Q, \tau)/d\tau^2] \).

**Solutions 5.7.1**

\[
\int_0^\pi P_x(\theta) (1 + \cos^2 \theta) \sin \theta \, d\theta \quad \text{with} \quad P_x(\theta) = 1
\]

\[
= \int_0^\pi \left[ \cos \theta + \frac{\cos^3 \theta}{3} \right] \sin \theta \, d\theta = \left[ \cos \theta - \frac{1}{3} \cos^3 \theta \right]_0^\pi = \frac{8}{3}.
\]

**5.7.2** \( \frac{dl}{dx} = -Tl \) so that \( \int_0^l \frac{dl}{l} = -T \int_0^l dx \). So \( \ln \left( \frac{l_f}{l_i} \right) = -Tl \)

from which eqn (5.7.4) follows immediately.

**5.7.3** \( K(\omega) = A_1 DQ^2/\left[ (\omega - \omega_0)^2 + (DQ^2)^2 \right] \). When \( \omega = \omega_0 \), \( K(\omega) = A_1 DQ^2 \).

The value of \( (\omega - \omega_0) = \Delta \omega_0 \) when \( K(\omega) \) is reduced to half. This value occurs when \( (\omega - \omega_0)^2 = (DQ^2)^2 \) since this doubles the denominator, i.e. \( (\omega - \omega_0) = \Delta \omega_0 = DQ^2 \).

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5.7.4

\[ R(0) = \frac{I}{I_0} \frac{r^2}{V_s} = \frac{9\pi^2}{3} \frac{n^2 - 1}{\lambda^2 (n^2 + 2)} \nu^2 N_p(0) \]

Putting \( \phi = N_p \nu \) and using (5.7.2) we have

\[ T = \frac{8\pi}{3} R_s(0) = \frac{8\pi}{3} \frac{9\pi^2}{\lambda^2 (n^2 + 2)} \phi \nu \]

\[ T/\phi = 24\pi \frac{(n^2 - 1)}{\lambda^2} \nu = H'\nu. \]

5.7.5

\[ \ln g^{(1)}(Q, \tau) = \sum_{n=1}^{\infty} K_n(Q) \left( \frac{-\tau}{n!} \right)^n = -\tau K_1(Q) + \frac{\tau^2}{2} K_2(Q) - \frac{\tau^3}{6} K_3(Q) \ldots \]

\[ \frac{d\ln g^{(1)}(Q, \tau)}{d\tau} = -K_1(Q) + \tau K_2(Q) - \frac{\tau^2}{2} K_3(Q) \ldots \]

\[ \lim_{\tau \to 0} \frac{d\ln g^{(1)}(Q, \tau)}{d\tau} = \lim_{\tau \to 0} \left\{ -K_1(Q) + \tau K_2(Q) - \frac{\tau^2}{2} K_3(Q) \ldots \right\} = -K_1(Q). \]

\[ \lim_{\tau \to 0} \frac{d^2\ln g^{(1)}(Q, \tau)}{d\tau^2} = \lim_{\tau \to 0} \left\{ K_2(Q) - \tau K_3(Q) \ldots \right\} = K_2(Q). \]

**Exercises.** 5.8.1 Verify eqn (5.8.3). Why is this average used and not simply \((1/r)\int v dr\)?

5.8.2 Establish eqn (5.8.4) by averaging over the inner part of the capillary. Verify eqns (5.8.5) and (5.8.6).
Solutions 5.8.1

\[
\bar{v} = \frac{\int_0^{r_0} 2\pi r v(r) dr}{\int_0^{r_0} 2\pi r dr} \quad \text{with} \quad v(r) = v_0 \left[1 - \left(\frac{r}{r_0}\right)^2\right]
\]

\[
\bar{v} = \frac{\int_0^{r_0} v(r) \left[1 - \left(\frac{r}{r_0}\right)^2\right] dr}{\int_0^{r_0} r dr} = \frac{v_0 \int_0^{r_0} \left[1 - r^2/r_0^2\right] dr}{r_0^{3/2}}
\]

\[
= v_0 \left[r_0^{3/2} - r_0^{4/2}/4r_0^2\right] / (r_0^{3/2}) = \frac{v_0}{2}.
\]

5.8.2

\[
\bar{v}_p = \frac{\int_0^{r_0} v(r) \left[1 - \left(r/r_0\right)^2\right] dr}{\int_0^{r_0} r dr} = \frac{v_0 \left[r_0^{3/2} - r_0^{4/2}/4r_0^2\right]}{(r_0 - a)^{3/2}}
\]

\[
= \frac{v_0 \left[1 - (r_0 - a)^2/2r_0^2\right]}{(r_0 - a)^{3/2}} = \frac{v_0 \left[1 - \frac{1}{2}(1 - \alpha)^2\right]}{(r_0 - a)^{3/2}}
\]

\[
= v_0 \left[1 - \frac{1}{2}(1 - \alpha)^2\right] = v_0 \left[1 - \frac{1}{2}(1 - \alpha)^2\right]
\]

\[
R = \frac{\bar{v}_p}{\bar{v}} = \frac{v_0 \left[1 - \frac{1}{2}(1 - \alpha)^2\right]}{v_0/2} = \frac{2 - (1 - \alpha)^2}{1 + \alpha(2 - \alpha)}
\]

\[
\Delta V = V \left[1 - \frac{1}{R_p}\right] = V \left[1 - \frac{1}{1 + \alpha(2 - \alpha)}\right] = V \frac{\alpha(2 - \alpha)}{1 + \alpha(2 - \alpha)}
\]

S5.11

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