Solutions

Chapter 11

Exercises 11.2.1. Establish eqn (11.2.4). [Note that the polarizability is sometimes defined in terms of the equation \( \rho = \alpha \varepsilon_0 E \) so that it has dimensions of volume. (Atkins 1978, p. 751; 1982, p. 772).]

11.2.2 Establish eqn (11.2.12) and note the similarity to eqn (11.2.4). Only the constant is missing from the simple formula.

Solutions 11.2.1

\[ V_{\text{int}}(R) = -p_1 p_2 / (4 \pi \varepsilon_0 R^2) \]  

(i) and \( p_1 = \alpha \varepsilon_0 \)  

(ii) \[ p_2 = \alpha \varepsilon_0 e^2 / (4 \pi \varepsilon_0 R^2) \]  

(iii) and hence:

\[ V_{\text{int}} = -\alpha \varepsilon_0^2 e^2 / (4 \pi \varepsilon_0 R^2) \]  

(iv) where \( \alpha = \varepsilon_0 / 8 \pi \varepsilon_0 \)  

(v) from eqn (11.2.1)

and \( \alpha = 4 \pi \varepsilon_0 \alpha_0 \)  

(vi) below eqn (11.2.3)

Rewriting (iv) as \( V_{\text{int}}(R) = -\alpha \varepsilon_0^2 e^2 / (4 \pi \varepsilon_0 R^2 \alpha_0) \)  

(vii) we can substitute \( \alpha / 4 \pi \varepsilon_0 \) for \( \alpha_0 \) from (vi) and \( 8 \pi \varepsilon_0 \varepsilon_0 \) for \( \varepsilon_0 / \alpha_0 \) from (v) to obtain:

\[ V_{\text{int}}(R) = 2 \alpha \varepsilon_0^2 h \nu / (4 \pi \varepsilon_0 R^2) \]  

(11.2.4)

11.2.2 \[ V_{\text{int}}(R) = -C_{\text{AB}} / R^6 \]  

with:

\[ C_{\text{AB}} = \left[ \frac{3 \varepsilon_0}{2m_e (4 \pi \varepsilon_0)^2} \right] \left( \alpha_A \alpha_B^0 \right)^{\frac{1}{3}} \alpha_A^0 / N_A \]  

from (11.2.9)

\[ = \frac{2 \left( e / m_e \right) \sqrt{3} \varepsilon_0 \alpha_A \alpha_B^0}{(\alpha_A^0 / N_A)^{\frac{1}{2}} + (\alpha_B^0 / N_B)^{\frac{1}{2}}} \]  

\[ = 3 \lambda \omega_0 \alpha_A \alpha_B^0 / 4 (4 \pi \varepsilon_0)^2 \]  

from eqn (11.2.11)

\[ = (3/4) \lambda \omega_0 R_0^6 \]  

from (11.2.10)

Therefore \( V_{\text{int}}(R) = -(3/4) \lambda \omega_0 R_0^6 / R^6 \)  

(11.2.12)

Exercises

11.3.1 Establish eqn (11.3.5)

11.3.2 Establish eqn (11.3.14) from (11.3.12). Also show that for two equal spheres of
radius $a$:

$$V_A = -\frac{A_{12}}{6} \left[ \frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \left( \frac{s^2 - 4}{s^2} \right) \right]$$

where $s = Ra$.

11.3.3 Establish eqn (11.3.15) and (11.3.16).

11.3.4 Verify Fig. 11.3.4 using $A_{13} = 3.70 \times 10^{-20}$ J for water.

11.3.5Plot the potential energy of a molecule as a function of distance $D$ from an infinite flat plate, using eqn (11.3.5) in the range $0 < D < 25$ nm. Take the molar volume as 20 cm$^3$ and estimate $C_{12}$ from eqn (11.2.4) using a reasonable value for the frequency $v$.

11.3.6 Plot the potential energy per unit area as a function of separation $L$ between two semi-infinite flat plates of a material for which $A = 6.0 \times 10^{-20}$ J in a fluid for which $A = 4.5 \times 10^{-20}$ J. (Make $1 < L < 25$ nm.)

11.3.7 Plot the function $V_A (H/A_{12})$ for two spheres of radius 100 nm and 150 nm in the range $0 < H < 25$ nm.

11.3.8 Establish eqn (11.3.24).

---

**Solutions 11.3.1**

\[
\Phi_{12}(D) = -C_{12} \rho_2 \int_0^\infty \frac{2\pi dr}{(D + x)^2 + r^2} = -C_{12} \rho_2 \int_0^\infty \frac{\pi dr}{(D + x)^2 + r^2} \]

\[
= -C_{12} \rho_2 \pi/2 \int_0^\infty \frac{1}{(D + x)^2 + r^2} dr = -(C_{12} \rho_2 \pi/2) \int_0^\infty (D + x)^4 \]

\[
= (C_{12} \rho_2 \pi/6) [(D + x)^5]_0^\infty = -C_{12} \rho_2 \pi/6 D^5
\]

11.3.2Examine the terms in eqn (11.3.12) separately:

\[
\frac{2a_1a_2}{R^2 - (a_1 - a_2)^2} = \frac{2a_1a_2}{(H + a_1 + a_2)^2 - (a_1 - a_2)^2} = \frac{2a_1a_2}{(H + 2a_1)(H + 2a_2)}
\]

\[
= \left( \frac{1}{H^2 + 2H(a_1 + a_2) + 4a_1a_2} \right) = \left( \frac{1}{[H/2a_1a_2] + 2H/a + 2} \right) = \frac{1}{2(h_5 + h_1 + 1)}
\]

S11.2

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\[
\frac{2a_1a_2}{R^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{(H + a_1 + a_2)^2 - (a_1 + a_2)^2} = \frac{2a_1a_2}{H[H + 2(a_1 + a_2)]} = \frac{1}{2H(1 + H/2(a_1 + a_2))}
\]

and in a similar way
\[
\frac{R^2 - (a_1 + a_2)^2}{R^2 - (a_1 - a_2)^2} = \frac{h_3 + h_1}{h_3 + h_1 + 1} = \frac{h_1(1 + h_2)}{1 + h_1 + h_3}
\]

since \(h_2 = h_3/h_1\).

Substituting these values gives eqn (11.3.14).

For \(a_1 = a_2 = a\) we have \(\bar{a} = a\) and so \(h_1 = s - 2\); \(h_2 = (s - 2)/4\); and \(h_3 = (s - 2)^3/4\).

\[
V_A = -A_{12} \frac{1}{12 (s-2)} \left[ \frac{4}{s+2} + \frac{s-2}{1 + (s-2) + (s-2)^3/4} + 2(s-2)\ln \left( \frac{(s-2)(1 + (s-2)/4)}{1 + (s-2) + (s-2)^3/4} \right) \right]
\]

\[
= -\frac{A_{12}}{12} \left[ \frac{4}{s+2} + \frac{4(s-2)}{s^2} + 2(s-2)\ln \left( \frac{s^2 - 4}{s^2} \right) \right] = \frac{A_{12}}{6} \left[ \frac{2}{s^2 - 4} + \frac{2}{s^2} \cdot \ln \frac{s^2 - 4}{s^2} \right]
\]

11.3.3 \(V_A(H) = -[A_{12}\bar{a}/12H][X + (H/\bar{a})Y + 2(H/\bar{a}) \ln(H/\bar{a})Z]\)

where \(X = [1 + H/2(a_1 + a_2)]^{-1} = 1 - H/(2(a_1 + a_2)) = 1 - (H/\bar{a})(2(a_1 + a_2))\),
\(Y = 1 + H/\bar{a} + H^2/4a_1a_2 = 1 + (H/\bar{a})(H/2(a_1 + a_2)) = 1\) and likewise \(Z = 1\).

Therefore \(V_A(H) = -[A_{12}\bar{a}/12H][1 - (H/\bar{a})(2(a_1 + a_2)) + H/\bar{a} + 2(H/\bar{a}) \ln H/\bar{a}...\]

For a sphere of radius \(a\) distance \(H\) from a planar halfspace: \(a_1 = a\) and \(\bar{a} = \infty\).

\[
\lim_{a_2 \to \infty} V_A(H) = -\frac{A_{12}\bar{a}}{6H} \left[ 1 + \frac{H/2\bar{a}}{1 + H/2\bar{a}} + \frac{H}{\bar{a}} \ln \left( \frac{H}{1 + H/2\bar{a}} \right) \right]
\]

\[
= -\frac{A_{12}\bar{a}}{6H} \left[ 1 + \frac{H}{2a + H} + \frac{H}{\bar{a}} \ln \left( \frac{H}{2a + H} \right) \right]
\]

S11.3
11.3.4 \[ A_{131} = (A_{11}^{\frac{1}{6}} - A_{33}^{\frac{1}{6}})^2 \] from eqn (11.3.24). For \( A_{33} = 3.70 \) units we have

<table>
<thead>
<tr>
<th>( A_{11} )</th>
<th>0</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>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{131} )</td>
<td>3.7</td>
<td>0.853</td>
<td>0.259</td>
<td>0.037</td>
<td>0.006</td>
<td>0.09777</td>
<td>0.277</td>
<td>0.522</td>
<td>0.819</td>
<td>1.159</td>
</tr>
</tbody>
</table>

11.3.5 \[ V_{im}(R) = -C_{AB}/R^6 \] with \( C_{AB} = 2\alpha^2 \hbar \nu/(4\pi \epsilon_0)^2 \) for two atoms.

\[ \rho_2 = 6.023 \times 10^{21}/20 \times 10^{21} = 30.1 \text{ molecules/nm}^3 \]

\[ \alpha/4\pi \epsilon_0 = a_0^3 = 1/\rho_2 \]

For a molecule approaching a half space we use eqn (11.3.5) and

\[ \phi_{12} = -\pi 2 (a_0)^6 \hbar \rho_2/6D^3 = -\pi 2 \times 6.626 \times 10^{-34} \times 10^{16}/(30.1 \times 6 \times D^3) \]

\[ = -0.23 \times 10^{20}/D^3 \] taking the frequency as \( 10^{16} \text{ Hz} \).

<table>
<thead>
<tr>
<th>( D )</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>12</th>
<th>16</th>
<th>20</th>
<th>25</th>
<th>nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -10^{22}\phi_{12} )</td>
<td>184</td>
<td>23.1</td>
<td>2.88</td>
<td>0.36</td>
<td>0.045</td>
<td>0.0133</td>
<td>0.0056</td>
<td>0.0029</td>
<td>0.00147</td>
<td>units for ( \phi_{12} ) are Joules</td>
</tr>
</tbody>
</table>

11.3.6 \[ E_A(L) = -A_{121}/12\pi L^2 \] with \( A_{121} = (A_{11}^{\frac{1}{6}} - A_{22}^{\frac{1}{6}})^2 - 1.08 \times 10^{-21} \text{ J.} \]

\[ E_A(L) = 2.86 \times 10^{-21}/L^2 \text{ J per unit area.} \]

<table>
<thead>
<tr>
<th>( L ) (nm)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -E_A(L) )</td>
<td>1.144</td>
<td>0.286</td>
<td>0.127</td>
<td>0.071</td>
<td>0.0458 \mu J/m^2</td>
<td></td>
</tr>
</tbody>
</table>

11.3.7 \[ H(nm) = 0 \]

| \( -V_A(H) \) | 1.525 | 0.633 | 0.359 | 0.233 | 0.163 |

11.3.8 \[ A_{132} = A_{12} + A_{33} - A_{13} - A_{32} \] from eqn (11.3.22)

\[ = A_{11}^{\frac{1}{6}} A_{22}^{\frac{1}{6}} + A_{33} - A_{11}^{\frac{1}{6}} A_{33}^{\frac{1}{6}} - A_{33}^{\frac{1}{6}} A_{22}^{\frac{1}{6}} \]

\[ = (A_{11}^{\frac{1}{6}} - A_{33}^{\frac{1}{6}})(A_{22}^{\frac{1}{6}} - A_{33}^{\frac{1}{6}}) \]

Exercise 11.4.1 Plot the correction factor \( f(p) \) (eqn (11.4.3)) as a function of \( p \) for \( 0 < p < 10 \).

Note the difference between this and \( F(p) \) of Fig. 11.4.1.
Solution 11.4.1

\[ \begin{array}{cccccc}
 p & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
 f(p) & 1.01 & 0.87 & 0.73 & 0.59 & 0.485 & 0.408 & 0.353 \\
 p & 7 & 8 & 9 & 10 \\
 f(p) & 0.308 & 0.274 & 0.247 & 0.225
\end{array} \]

Exercises. 11.5.1. Use eqn (11.5.5) to show that the van der Waals interaction energy of two large spheres of radii \( a_1 \) and \( a_2 \) in the limit \( H \ll a_j \) is given by

\[ V_A(H) = \left( \frac{2a_1 a_2}{a_1 + a_2} \right) \frac{A_{12}}{12H}. \]

Note that this corresponds to taking only the first term in the expression (11.3.15).

Solution 11.5.1 From eqn (11.5.5) substituting for \( \sqrt{\lambda_1 \lambda_2} \):

\[ V_A(H) = \frac{2 \pi a_1 a_2}{a_1 + a_2} \int_0^H - \frac{A_{12}}{12 \pi L^2} \, dL = \frac{a_1 a_2}{a_1 + a_2} \left[ - \frac{A_{12}}{6L} \right]_H^0 = \left( \frac{2a_1 a_2}{a_1 + a_2} \right) \frac{A_{12}}{12H}. \]

\[ F(H) - 2 \pi (\lambda_1 \lambda_2)^{1/2} E(H) \text{ from eqn (11.5.7)} = 2 \pi \sqrt{\lambda_1 \lambda_2} E(H) \text{ from (11.5.9)}. \]

Exercises. 11.6.1 Verify that eqn (11.6.6) is a solution of eqn (11.6.4) if \( \epsilon(\omega) \) is given by eqn (11.6.5).

11.6.2. Consider the dielectric response function:

\[ \epsilon(\omega) = \epsilon_0 \left( 1 + \frac{d}{1 - i \omega \tau} + \frac{f}{\omega_0^2 - \omega^2 - i \omega \omega} \right) \]

and convert it into \( \epsilon'(\omega) = \epsilon_r(\omega) + i \epsilon_i(\omega) \) for real \( \omega \). (\( \epsilon' \) and \( \epsilon \) must both be real functions.)

11.6.3. Establish eqn (11.6.15) from eqn (11.6.14).

11.6.4 Use the series expansion for \( \ln(1-p) = \sum_1^\infty (-p)^n/n \) for \( 0 < p < 1 \)

\[ \int_0^\infty x \ln[1 - a \exp(-x)] dx = -\sum_{n=1}^\infty a^n/n^3. \]

S11.5
(Compare eqn 11.6.30).

**Solutions 11.6.1**

\[ (1 + \epsilon(\omega))^2 = (1 + 1 + f/(\omega_0^2 - \omega^2))^2 = 0 \quad \text{so} \quad \frac{2 (\omega_0^2 - \omega^2) + f}{f} = 0 \]
\[ \omega = \sqrt{\omega_0^2 + f/2} \]

11.6.2 \( \epsilon(\omega) = 1 + d/(1 - i\omega) + f/(\omega_0^2 - \omega^2 - ig\omega) \)
\[ = 1 + d(1 + i\omega)/(1 + \omega^2 \tau^2) + f(\omega_0^2 - \omega^2 + ig\omega)/(\omega_0^2 - \omega^2 + g^2 \omega^2) \]
\[ = 1 + \frac{d}{1 + \omega^2 \tau^2} + \frac{f(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + g^2 \omega^2} + i\omega \left[ \frac{dx}{1 + \omega^2 \tau^2} + \frac{f g}{(\omega_0^2 - \omega^2)^2 + g^2 \omega^2} \right] \]

\(- \epsilon(\omega) + i\epsilon(\tau(\omega)) \)

11.6.3

\[ \ln\left( \sum_{n=0}^{\infty} \exp[-(n+1/2)\hbar \omega/jT] = \ln \left( \exp(-\hbar \omega/2jT) \sum_{n=0}^{\infty} \exp(-\hbar \omega/jT) \right) \right) \]
\[ = \ln \left[ \frac{\exp(-\hbar \omega/2jT)}{1 - \exp(-\hbar \omega/jT)} \right] = \ln \left[ \frac{1}{\exp(\hbar \omega/2jT) - \exp(-\hbar \omega/2jT)} \right] \]
\[ = -\ln[2 \sinh(\hbar \omega/2jT)]. \]

11.6.4

\[ \int_0^\infty \ln[1 - a \exp(-x)] \, dx = \int_0^\infty \left[ x \sum_{s=1}^{\infty} \frac{a \exp(-x)}{s} \right] \, dx = -\sum_{s=1}^{\infty} \int_0^\infty \frac{x (ae^{-x})^s}{s} \, dx \]
\[ = -\sum_{s=1}^{\infty} \frac{a^s}{s} \int_0^\infty \exp(-sx) \, dx = -\sum_{s=1}^{\infty} \frac{a^s}{s} \left[ \frac{1}{s} \int_0^\infty \frac{dx}{e^{-sx}} \right] \]
\[ = \sum_{s=1}^{\infty} \frac{a^s}{s^2} \left[ \left. x \exp(-sx) \right|_0^\infty - \int_0^\infty \exp(-sx) \, dx \right] = \sum_{s=1}^{\infty} \frac{a^s}{s^2} \left( \frac{1}{s} \left[ \exp(-sx) \right]_0^\infty \right) = -\sum_{s=1}^{\infty} \frac{a^s}{s^3} \]

S11.6
Exercises 11.7.1 Establish equations (11.7.7), (11.7.8) and (11.7.9).

Solution 11.7.1

\[ \varepsilon''(\omega) = \sum_{k=1}^{N} f_k \delta(\omega - \omega_k) \quad \text{and} \quad \varepsilon''(\omega) = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{\omega}{\omega^2 + \xi^2} \varepsilon''(\omega) d\omega \]

so \[ \varepsilon''(\omega) = 1 + \frac{2}{\pi} \sum_{k=1}^{N} f_k \frac{\omega}{\omega_k^2 + \xi^2} \delta(\omega - \omega_k) d\omega \]

\[ = 1 + \frac{2}{\pi} \sum_{k=1}^{N} f_k \frac{\omega_k}{\omega_k^2 + \xi^2} \quad \text{from eqn (11.7.6)} = 1 + \frac{2}{\pi} \frac{c_k}{1 + (\omega/\omega_k)^2} \]

where \( c_k = 2f_k/\pi\omega_k \).

\[ \varepsilon'(\omega) = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{\omega \varepsilon''(\omega) d\omega}{\omega^2 + \omega_k^2} \] and \[ \varepsilon''(\omega) = \sum_{k=1}^{N} f_k \delta(\omega - \omega_k) \]

\[ \varepsilon'(\omega) = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{\omega \varepsilon''(\omega) d\omega}{\omega^2 + \omega_k^2} \delta(\omega - \omega_k) d\omega = 1 + \frac{2}{\pi} \sum_{k=1}^{N} \frac{f_k \omega_k}{\omega_k^2 + \omega^2} \]

\[ = 1 + \sum_{k=1}^{N} \frac{c_k}{1 - (\omega/\omega_k)^2} \]

The symbol \( P \) refers to the principal value of the integral (eliminating the region around \( \omega_k \) where the integral diverges.)

Exercises. 11.9.1 Use the data in Table 11.2 to estimate theoretical values of \( \cos \theta \) for hydrocarbons with 6, 8, 10, 12, 14 and 16 carbons and compare your results with those shown in Fig. 11.9.2.

11.9.2 Given the following data for the interfacial tension \( \gamma_{12} \) between water and various hydrocarbons, estimate \( \gamma_w \).
<table>
<thead>
<tr>
<th>$n = $</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>10</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1 (\text{C}<em>n\text{H}</em>{2n+2}) \text{ (mN m}^{-1}\text{)}$</td>
<td>18.4</td>
<td>20.4</td>
<td>21.8</td>
<td>23.9</td>
<td>25.6</td>
</tr>
<tr>
<td>$\gamma_{12} \text{ (mN m}^{-1}\text{)}$</td>
<td>51.1</td>
<td>50.2</td>
<td>50.8</td>
<td>51.2</td>
<td>52.2</td>
</tr>
</tbody>
</table>

**Solutions**

11.9.1 From eqn (11.9.7), for $n = 7$: $\cos \theta = -1 + 2(3.8/4.32)^{1/2} = 0.88$ so that $\theta = 29^\circ$. For $n = 10$, $\cos \theta = 0.78$ so that $\theta = 39^\circ$ etc.

11.9.2 From the analogue of eqn (11.9.5) with $\gamma_w$ replacing $\gamma_M$ we can rearrange to give:

$$\gamma_w^d = (\gamma_{12}^c + \gamma_w^c - \gamma_{\text{w/HC}}^c)^{1/2}$$

and substituting gives the following estimates for $\gamma_w^d$:

21.85; 22.66; 22.00; 21.66; 20.84, so that $\gamma_w^d = 21.6 \pm 0.7 \text{ N m}^{-1}$. 

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Solutions
Chapter 12

Exercises. 12.2.1 Show that the free energy change involved in arranging the diffuse counter charge is zero if the ions obey the Boltzmann equation.

12.2.2 Establish eqn (12.2.4) using the appropriate form of eqn (7.3.27).

12.2.3 Show that at low potentials, where the Debye-Hückel approximation holds, the free energy of a flat double layer is $\Delta F = -\frac{1}{2} e \kappa \psi_0^2$ and of a sphere is $-2\pi \varepsilon_0 a (1 + \kappa a) \psi_0^2$.

Solutions

12.2.1 $\Delta F = \Delta U = -T \Delta S = z, e \psi - T k \ln n_i^0/n_e$. But $n_i^0 = n_i^0 \exp (-z_i e \psi/kT)$

$\therefore \Delta F = z_i e \psi - kT [z_i e \psi/kT] = 0$.

12.2.2

$\Delta F = -\int \sigma_0 \delta \psi_0' = \int \frac{\psi_0}{4\pi \varepsilon_0} \sinh \left( \frac{z e \psi_0'}{2kT} \right) d\psi_0' = \left[ \frac{4\pi \varepsilon_0 e}{\kappa} \frac{2kT}{2kT} \cosh \left( \frac{ze \psi_0'}{2kT} \right) \right] \psi_0$

$= -\frac{8\pi \varepsilon_0 kT}{\kappa} \left[ \cosh \left( \frac{ze \psi_0}{2kT} \right) - 1 \right]$ from eqn (12.2.3)

12.2.3

$\Delta F = -\int \psi_0 \delta \psi_0' = -\int \varepsilon_0 \kappa \psi_0' d\psi_0' = \int \frac{\varepsilon_0 \kappa \psi_0'}{2} \delta \psi_0' = \frac{e \kappa \psi_0^2}{2}$ from eqn (7.3.29)

$\therefore \Delta F = -\frac{1}{2} \sigma_0 \psi_0$ since $\sigma_0 = e \kappa \psi_0$

For a sphere $\Delta F = -\int \rho_0 \delta \psi_0' = -\int 4\pi \varepsilon_0 [1 + \kappa a] \psi_0' d\psi_0'$ from eqn (7.11.6).

$= -4\pi \varepsilon_0 [1 + \kappa a] \psi_0^2/2 = -2\pi \varepsilon_0 (1 + \kappa a) \psi_0^2$

Exercises. 12.3.1 Calculate the potential energy of repulsion $V_R$ as a function of separation $(0 \leq D \leq 20 \text{ nm})$ for two flat plates of surface potential $51.4 \text{ mV}$ in a $2:2$ electrolyte at a concentration of $10^{-4} \text{ M}$ in water at 298 K.
12.3.2 Establish eqn (12.3.5) and integrate it to obtain eqn (12.3.6) using the boundary condition \( \frac{dy}{dx} = 0 \) at \( X = 0 \) and \( y = y_m \).

12.3.3 Establish eqns (12.3.7) and (12.3.8)

12.3.4 Expand the cosh term in eqn (12.3.4) as a power series to establish eqn (12.3.12). Hence establish eqn (12.3.14).

12.3.5 Integrate the Debye-Hückel equation \( \frac{d^2 \psi}{dx^2} = \kappa \psi \) with the appropriate boundary conditions to obtain \( \frac{d\psi}{dx} = \kappa (\psi^2 - \psi_m^2)^{1/2} \). Use the substitution \( \psi = \psi_m \cosh \omega \) to perform the second integration and hence show that \( \psi_0 = \psi_m \cosh \kappa D/2 \).

12.3.6 Use eqn (12.3.12) along with the result of Exercise (12.3.5) and eqn (12.2.7) to establish eqn (12.3.16).

12.3.7 Calculate the value of \( V_R \) from eqn (12.3.17) for the same conditions as in Exercise 12.3.1 and plot the results on the same graph.

12.3.8 Show that for small \( \psi_0 \) (in the Debye-Hückel approximation) the potential profile between two flat plates may be written (for large \( D \)):

\[
\psi(x) = \psi_0 \frac{\cosh[\kappa(D/2 - x)]}{\cosh(\kappa D/2)} \quad \text{where} \quad x = 0 \text{ on one plate.}
\]

12.3.9 Show that if the Debye-Hückel approximation holds throughout the region between two approaching flat plates then \( V_R = 2e\kappa \psi_0^2 \exp( - \kappa D ) \) if the surface potential is constant during the interaction.

12.3.10 Use eqns (8.7.3) and (8.7.4) to derive eqn (12.3.2) for the osmotic pressure between two identical charged flat plates in the form: \( p = p_m = (e/2)(d\psi/dx)^2 \) where \( p_m \) is the pressure in the midplane and \( p \) is the osmotic pressure elsewhere.

### Solutions 12.3.1

\[
y_0 = 2e\psi_0/kT = 2 \times 1.6 \times 10^{-19} \times 0.0514 / 1.38 \times 10^{-23} \times 298 = 4.00
\]

From Table 12.1

\[
\begin{array}{cccccccc}
\psi_{\text{max}} & \psi_0 & 8.07 & 6.51 & 4.97 & 3.5 & 1.26 & 0.26 & 0.06 & 0.015 & 0.0023 \\
\kappa D & 0 & 0.1782 & 0.3360 & 0.5384 & 0.8210 & 1.768 & 3.404 & 4.924 & 6.326 & 8.214 \\
D(\text{nm}) & 0 & 2.71 & 5.109 & 8.187 & 12.48 & 26.89 & 51.76 & 74.88 & 96.75 & 124.9 \\
V_R(\mu J \cdot m^{-2}) & 166.5 & 132.7 & 107.0 & 81.71 & 57.54 & 20.7 & 4.27 & 0.99 & 0.25 & 0.038 \\
\kappa & 3.288 \sqrt{J} \text{ nm}^{-1} \text{ from eqn (7.3.14)} & L = \frac{1}{2} \sum_c \zeta_i = \frac{1}{2}(10^{-4} \times 4 + 10^{-4} \times 4) = 4 \times 10^{-4} \\
\kappa & = 6.575 \times 10^7 \text{ m}^{-1} \quad V_R = (\kappa/2)^2 f = 1.644 \times 10^7 \times 10^{-12} \mu J \cdot m^{-2} = 16.44 \mu J \cdot m^{-2}.
\end{array}
\]

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12.3.2 From eqn (12.3.1): \[ \frac{d^2\psi}{dx^2} = \left(2n^2ze^2/e\right) \sinh \left[z\epsilon\psi/kT\right]. \] Putting \( y = z\epsilon\psi/kT \) then:

\[ \frac{dy}{dx} = \left[ze/kT\right] \frac{d\psi}{dx} \text{ and } d^2y/dx^2 = \left[ze/kT\right] d^2\psi/dx^2. \]

So \( [kT/ze^2] d^2y/dx^2 = \left(2n^2ze^2/e\right) \sinh y. \) Hence \( [kT/2n^2ze^2] \) \( d^2\psi/dx^2 = \left(1/\kappa^2\right) d^2\psi/dx^2 = \sinh y. \)

Putting \( X = \kappa x \) then \( dX = \kappa dx \) and \( d^2y/dX^2 = \left(1/\kappa^2\right) d^2y/dx^2 = \sinh y. \)

\[ 2 \frac{dy}{dX} \frac{d^2y}{dX^2} = 2 \sinh y \frac{dy}{dX} \quad \text{(cf section 7.3).} \]

So \[ \int_0^X \frac{d}{dX} \left[ \frac{dy}{dX}\right]^2 \] \( dX = 2 \int_{y_m}^y \sinh y \, dy \]

\[ \left. \frac{dy}{dX} \right|_0^X \sinh y \] \( = 2 \cosh \frac{y}{y_m}. \)

\( dy/dX = \text{sgn} (y_m) \left[2 \left(\cosh y - \cosh y_m\right)\right]^{\frac{1}{2}}. \)

This solution places the origin in the centre between the plates. The function \( \text{sgn}(y_m) = y/y_m \) \( \text{will be } +1 \text{ for } y_m > 0 \text{ and } -1 \text{ for } y_m < 0. \) For \( y_m > 0, \) therefore, \( dy/dX \) is positive and \( y \) increases with \( X. \) This expression gives only one half of the solution: the other half is obtained by symmetry.

12.3.3 \( \frac{dy}{dX} = \text{sgn} (y_m)Q \) from eqn (12.3.6); \( dQ/dy = [1/\text{sgn}(y_m)] \frac{d}{dy} \frac{dy}{dX} \)

\[ \frac{dQ}{dy} = \frac{1}{\text{sgn}(y_m)} \frac{dX}{dy} \frac{dy}{dX} = \frac{1}{\text{sgn}(y_m)^2} \frac{d^2y}{dX^2} = \frac{\sinh y}{Q} \quad \text{.........from (12.3.5)} \]

But \( Q^2 = 2(\cosh y - \cosh y_m) \) from (12.3.6) so \( \cosh y = Q^2/2 + \cosh y_m \)

and \( \sinh y = (\cosh^2 y - 1)^{\frac{1}{2}} = \text{sgn} (y_m) \left[\left(Q^2/2 + \cosh y_m\right)^2 - 1\right]^{\frac{1}{2}} \)

Substituting in eqn (1) above gives eqn (12.3.7).

Then \( dX/dQ = [dX/dy][dy/dQ] = [1/\text{sgn}(y_m) Q] Q/\sinh y. \)

\[ = \frac{1}{\left(\text{sgn}(y_m)\right)^{\frac{1}{2}} \left[\left(Q^2/2 + \cosh y_m\right) - 1\right]^{\frac{1}{2}}} \]

12.3.4 \( \bar{p} = 2n^2kT/\left(\cosh y_m - 1\right) \)

S12.3

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\[
\cosh y = \frac{\exp y + \exp(-y)}{2} = \frac{1 + y + \frac{y^2}{2} + (1 - y + \frac{y^2}{2})}{2} = 1 + \frac{y^2}{2}
\]

\[
\therefore \bar{p} = n^0 k T y_m^2 = [n^0 k T z^2 e^2/k^2 T^2] \psi_m^2 = \frac{\kappa^2 e}{2} \psi_m^2
\]

\[
V_R = -\int_{-\infty}^{\infty} \bar{p} \, dD = -\int_{-\infty}^{\infty} \frac{\kappa^2 e}{2} \psi_m^2 \, dD = -\frac{\kappa^2 e}{2} \int_{-\infty}^{\infty} \frac{64 k^2 T^2}{z^2 e^2} z^2 \exp(-\kappa D) \, dD \quad \text{from (12.3.13)}
\]

\[
V_R = +\frac{\kappa^2 e}{2} \cdot \frac{64 k^2 T^2}{z^2 e^2} \cdot Z^2 \cdot \frac{1}{\kappa} \left[ \exp(-\kappa D) \right]_{D}^{D/2} = \frac{64 n^0 k T Z^2}{\kappa} \exp(-\kappa D)
\]

12.3.5 \[d^2 \psi / dx^2 = \kappa^2 \psi; \quad \int 2 (d \psi / dx) (d^2 \psi / dx^2) \, dx = \int 2 \kappa^2 \psi (d \psi / dx) \, dx \]

\[d \psi / dx = \kappa \sqrt{\psi^2 - \psi_m^2} ; \quad \int \psi_m \sqrt{\psi^2 - \psi_m^2} \, dx = \int \kappa \, dx = \kappa D / 2 \]

Put \(\psi = \psi_m \cosh W\). Then \(d \psi = \psi_m \sinh W \, dW\)

\[
\int_{\psi_m}^{\psi_m} \frac{\psi_m \sinh W \, dW}{\sqrt{\psi_m^2 (\cosh^2 W - 1)}} = \int dW = W = \cosh^{-1} \left[ \frac{\psi}{\psi_m} \right] - \cosh^{-1} 1 = \cosh^{-1} [\psi / \psi_m]
\]

That is: \(\psi / \psi_m = \cosh (\kappa D / 2)\)

12.3.6 \[\bar{p} = [\kappa^2 e / 2] \psi_m^2 \quad \text{so} \quad V_R = \int \bar{p} \, dD = -\int [\kappa^2 e \psi_m^2 / 2] \, dD \]

S12.4
\[ V_R = -\frac{\kappa^2 e^2}{2} \int_D \frac{dD}{-\cosh^2(\kappa D/2)} = \frac{\kappa^2 e^2}{2} \int_D \frac{dD}{\text{sech}^2(\kappa D/2)} \]

\[ = -\kappa e \psi_0 \left[ \tanh \frac{\kappa D}{2} \right] = \kappa e \psi_0^2 \left[ 1 - \tanh(\kappa D/2) \right] \]

\[ = \frac{2\eta k^2e^2}{\epsilon kT} \left[ 1 - \tanh(\kappa D/2) \right] = \frac{2\eta k^2T}{\kappa} \psi_0^2 \left[ 1 - \tanh(\kappa D/2) \right] \text{ eqn}(12.3.16) \]

\[ V_R = \frac{2\eta kT}{\kappa} \psi_0 \left[ \frac{\exp(\kappa D/2) + \exp(-\kappa D/2)}{\exp(\kappa D/2) + \exp(-\kappa D/2)} \right] \]

\[ = \frac{2\eta kT}{\kappa} \psi_0 \left[ \frac{2\exp(-\kappa D/2)}{\exp(\kappa D/2) + \exp(-\kappa D/2)} \right] = \frac{4\eta kT}{\kappa} \psi_0 \left[ \frac{\exp(-\kappa D)}{1 + \exp(-\kappa D)} \right] \]

12.3.7 \[ \psi_0 = 4; \frac{2}{\kappa} = \tanh(\psi_0/4) = 0.7616; \quad C = 10^{-4} \text{ M.} \quad \eta^0 = 6.022 \times 10^{23} \times 10^{-1} \text{ ions/m}^3 \]

\[ \kappa = 6.576 \times 10^{-3} \text{ m} \]

So \[ V_R = [32 \times 6.0225 \times 10^{22} \times 1.38 \times 10^{-33} \times 298] \times (0.7617)^2 \times [1 - \tanh(\kappa D/2)] / 6.576 \times 10^{-7} \]

\[ = 6.991 \times 10^{-9} [1 - \tanh(\kappa D/2)] \text{ J/m}^2 \]

\[ \psi D \quad 0 \quad 0.1782 \quad 0.336 \quad 0.5384 \quad 0.8210 \quad 1.768 \quad 3.404 \quad 4.924 \quad 6.362 \quad 8.214 \]

\[ \tanh(\kappa D/2) \quad 0 \quad 0.0889 \quad 0.1664 \quad 0.2628 \quad 0.3889 \quad 0.7084 \quad 0.936 \quad 0.986 \quad 0.997 \quad 0.9995 \]

\[ V_R \text{ (mJ/m}^2) \quad 69.9 \quad 63.7 \quad 58.27 \quad 51.53 \quad 42.72 \quad 20.38 \quad 4.50 \quad 1.009 \quad 0.2409 \quad 0.0379 \]

12.3.8 Proceeding as in exercise (12.3.5) we have: \[ d^2\psi/dx^2 = \kappa^2 \psi \] and hence:

\[ d\psi/dx = -\kappa(\psi^2 - \psi_m^2)^{1/2} \] Then:

\[ \int_{\psi}^{\infty} \frac{d\psi}{(\psi^2 - \psi_m^2)^{1/2}} = \int_{\kappa x}^{\infty} d\kappa = \kappa x. \]

Proceeding as in exercise (12.3.5) putting \( \psi = \psi_m \cosh W \) we get:

\[ \cosh^{-1}[\psi/\psi_m] - \cosh^{-1}[\psi/\psi_m] - \cosh^{-1}(\psi/\psi_m) - \kappa D/2 = -\kappa x. \] Thus \( \psi/\psi_m = \cosh[\kappa(D/2 - x)] \)

and \( \psi = \psi_0 \{ \cosh[\kappa(D/2 - x)] / \cosh(\kappa D/2) \} \) again using exercise (12.3.5).

12.3.9 If \( \psi = \psi_0 \exp(-\kappa x) \) near an isolated plate then, assuming additivity:

S12.5
\[ \psi_m = 2\psi_0 \exp(-\kappa D/2). \]

Then \( \bar{p} = \kappa^2 \epsilon \psi_m^2/2 \) from eqn (12.3.12) = \( 2\kappa^2 \epsilon \psi_0^2 \exp(-\kappa D) \).

Then \( V_R = -\int \bar{p} \, dD = -[-2\kappa \epsilon \psi_0^2 \exp(-\kappa D)]_\infty^D = 2\kappa \epsilon \psi_0^2 \exp(-\kappa D) \).

12.3.10 When the plates have been brought to a certain separation and all flow has ceased, we have from eqn (8.7.4): \( \nabla p = -\sum \epsilon_j z_j \, \nabla \psi \) and from eqn (8.7.3):

\[ \nabla^2 \psi = -\sum \epsilon_j z_j \, \epsilon / \epsilon. \]

In this case both the pressure and the potential vary only in one dimension so

\[ \frac{dp}{dz} = -\sum \epsilon_j z_j \, d\psi/dz \]

and \( d^2 \psi/dz^2 = -(1/\epsilon) \sum \epsilon_j z_j \, \alpha = -(1/\epsilon) \sum \epsilon_j z_j \, \epsilon_0 \exp(-z_j \psi/kT) \).

The second eqn can be integrated as we did for eqn (7.3.17) to give:

\[ (d\psi/dz)^2 = [4n_0^2 kT/\epsilon] \int \sinh y \, dy \text{ where } y = z \psi/kT \text{ so} \]

\[ [e/2](d\psi/dz)^2 = 2n_0^2 kT \cosh y - \rho_m \text{ where } \rho_m = 2n_0^2 kT \cosh \gamma_m \text{ which is (12.2.3)} \]

Note that, for a symmetrical electrolyte from eqn (8.7.4):

\[ \frac{dp}{dz} = \frac{d\psi}{dz} \left( -z \varepsilon_0 \exp(-z \psi/kT) + z \varepsilon_0 \exp(z \psi/kT) \right) = 2 z \varepsilon_0 \sinh(z \psi/kT) \frac{d\psi}{dz} \]

and integrating between the appropriate limits gives:

\[ p - p_m = 2 kT \varepsilon_0 \int \sinh(z \psi/kT) \, d(z \psi/kT) = 2 kT \varepsilon_0 \left[ \cosh(z \psi/kT) \right]_{-\infty}^{\psi_0} \]

which gives eqn (12.3.4).

**Exercises.**

12.4.1 If the approaching plates are of opposite sign of potential the control plate must have potential \( -\psi_m \) and the potential in the midplane is then zero. Discuss the resulting forces in terms of the Maxwell stress in the region between the plates (refer to Hunter 1975).

12.4.2 Verify that eqn (12.4.8) is a general solution for eqn (12.4.7). (Compare the result of Exercise 12.3.5). Derive eqns (12.4.9-11).

12.4.3 Establish eqns (12.4.13-15).

12.4.4 Verify that \( V_R^\Psi = 0 \) for \( \psi_{01} = 25 \text{ mV} \) and \( \psi_{02} = 50 \text{ mV} \) for \( \kappa D = 0.2 \).

12.4.5 The force between two flat plates is given by \( F = -dV_R/dD \). Use eqn (12.4.15) to show that:

\[ F = -\frac{1}{2} \epsilon \kappa^2 [(\psi_{01}^2 + \psi_{02}^2) \coth \kappa D - 2 \psi_{01} \psi_{02} \coth \kappa D] \sinh \kappa D \]

and hence prove that \( F = 0 \) when \( \psi_{02} = \psi_{01} \exp(\pm \kappa D) \) (i.e., plate 1 cannot ‘see’ plate 2 if the potential there is the same as it would be for an isolated plate).

12.4.6 Show that for any value of \( \kappa D \), eqn (12.4.15) reduces to

\[ V_R^\Psi = \epsilon \kappa \psi_0^2 [1 - \tanh(\kappa D/2)] \]

when \( \psi_{01} = \psi_{02} = \psi_0 \).

S12.6

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Solutions 12.4.1 See the reference to the literature. The midplane potential is only zero if the plates each have the same potential and it is important to note that the Maxwell stress in this case is not in general zero. (See Figure (redrawn from Hunter (1975).) The curve marked SP (single plate) corresponds to the potential fall-off if the second plate is not there. The presence of the second plate with opposite charge in this case, causes the potential to fall of more quickly between the plates. If the two plates are of different potential one can again use the method of isodynamic curves as in Figure 12.4.1 except that one side of that figure is reflected in the horizontal plane and the free energies are subtracted in this case.

When the plates have opposite sign but numerically equal potentials the potential in the midplane is zero so the osmotic pressure is also zero there. The (attractive) force between the plates at that distance is then due to the Maxwell stress.

12.4.2 \[ \psi(x) = A_1 \cosh \kappa x + A_2 \sinh \kappa x; \quad \frac{d\psi}{dx} = \kappa A_1 \sinh \kappa x + \kappa A_2 \cosh \kappa x; \]
\[ \frac{d^2\psi}{dx^2} = \kappa^2 A_1 \cosh \kappa x + \kappa^2 A_2 \sinh \kappa x = \kappa^2 \psi(x). \]

Since \( \cosh \) and \( \sinh \) are linearly independent and the solution has the necessary two independent parameters (for a second order D.E.) it is sufficiently general. The earlier solution is \( B_1 \exp(\kappa x) + B_2 \exp(-\kappa x) \) and this one can be written \( A_1[\exp(\kappa x) + \exp(-\kappa x)]/2 + A_2[\exp(\kappa x) - A_2 \exp(-\kappa x)]/2 = 1/2(A_1 + A_2) \exp(\kappa x) + 1/2(A_1 - A_2) \exp(-\kappa x) \) so \( A_1 + A_2 = 2B_1 \) and \( A_1 - A_2 = 2B_2 \).

\[ \psi_{0,1} = A_1 \quad \psi_{0,2} = A_1 \cosh \kappa D + A_2 \sinh \kappa D. \]

S12.7
\[ \psi = \psi_{0,1} \cosh \kappa x + \left[ \frac{\psi_{0,2} - \psi_{0,1} \cosh \kappa D}{\sinh \kappa D} \right] \sinh \kappa x \]

\[ \frac{d\psi}{dx} = \kappa \psi_{0,1} \sinh \kappa x + \left[ \frac{\psi_{0,2} - \psi_{0,1} \cosh \kappa D}{\sinh \kappa D} \right] \kappa \cosh \kappa x. \]

Therefore at \( x = 0 \) \[ \left( \frac{d\psi}{dx} \right)_{x=D} = \kappa \psi_{0,1} \sinh \kappa D + \kappa \left[ \psi_{0,2} \coth \kappa D - \psi_{0,1} \frac{\cosh^2 \kappa D}{\sinh \kappa D} \right] \]

\[ = \kappa \psi_{0,1} \left[ \frac{\sinh^2 \kappa D - \cosh^2 \kappa D}{\sinh \kappa D} \right] + \kappa \psi_{0,2} \coth \kappa D = \kappa (\psi_{0,2} \coth \kappa D - \psi_{0,1} \cosech \kappa D) \]

12.4.3 \( \Delta F(D) = -\frac{1}{2} \langle \hat{D}_1 \psi_{0,1} + \sigma_2 \psi_{0,2} \rangle \) [eqn. (12.4.6)] and substituting from eqn (12.4.12):

\[ \Delta F(D) = \frac{1}{2} \kappa \psi_{0,1} \psi_{0,2} \cosech \kappa D - \psi_{0,1} \coth \kappa D - \psi_{0,2} \coth \kappa D + \psi_{0,1} \psi_{0,2} \cosech \kappa D \]

\[ = \frac{1}{2} \kappa \psi_{0,1} \psi_{0,2} \cosech \kappa D - (\psi_{0,1}^2 + \psi_{0,2}^2) \coth \kappa D \]

which is eqn (12.4.13).

If \( D \) is large enough cosech \( \kappa D = 1/\sinh \kappa D \) = 0 and coth \( \kappa D = 1 \) so that:

\[ \Delta F(\omega) = -\frac{1}{2} \kappa \psi_{0,1} \psi_{0,2} \cosech \kappa D \]

which is eqn (12.4.14).

Then \( V_R = [\Delta F(D) - \Delta F(\omega)] = \frac{1}{2} \kappa \psi_{0,1} \psi_{0,2} \left[ 1 - (1 - \coth \kappa D) + 2 \psi_{0,1} \psi_{0,2} \cosech \kappa D \right] \]

which is eqn (12.4.15).

12.4.4 Substituting in the bracketed expression in eqn (12.4.15)\( \psi_{0,1} = 0.025, \psi_{0,2} = 0.050, \kappa D = 0.2 \) we have:

\[ 3.125 \times 10^{-3} (1 - 5.076) + 2.5 \times 10^{-3} \times 4.967 = 1.271 \times 10^{-2} + 1.242 \times 10^{-2} \]

\[ \approx -3 \times 10^{-4} \text{ V}^2. \] (Obviously the two terms come near to cancelling one another at this point.)

12.4.5 Note first that \( \text{d}(\cosech x)/dx = \text{d}(1/\sinh x)/dx = -\cosh x/\sinh^2 x \)

\[ = -\coth x/\sinh x = -\coth x \cdot \cosech x. \]

\( \text{d}(\coth x)/dx = [\cosh x/\sinh x] = -[\cosh^2 x/\sinh^2 x] + 1 = -\cosech^2 x. \)

Now \( F = -\text{d}V_R/\text{d}D = -\frac{1}{2} \kappa \psi_{1,1} \psi_{1,2} (\kappa \cosech^2 \kappa D) - 2 \psi_{1,1} \psi_{1,2} \kappa \coth \kappa D \cdot \cosech \kappa D \)

S12.8
\[-\frac{1}{2}\varepsilon \kappa^2 \left[ \left( \psi_1^2 + \psi_2^2 \right) \coth \kappa D - 2 \psi_1 \psi_2 \coth \kappa D \right] \coth \kappa D \]

which is the required equation. Then \( F = 0 \) when

\[
\left[ \frac{\psi_1^2 + \psi_2^2}{2 \psi_1 \psi_2} \right] = \frac{\coth \kappa D}{\coth \kappa D} = \coth \kappa D \quad \text{so} \quad \psi_2^2 - (2\psi_1 \cosh \kappa D)\psi_2 + \psi_1^2 = 0
\]

\[
\psi_2 = -\frac{2\psi_1 \cosh \kappa D \pm \sqrt{4\psi_1^2 \cosh^2 \kappa D - 4\psi_1^2}}{2} = \psi_1 \cosh \kappa D \pm \psi_1 \sinh \kappa D
\]

\[-\psi_1 (\cosh \kappa D \pm \sinh \kappa D) = \psi_1 \exp(\pm \kappa D)\]

12.4.6 Putting \( \psi_1 = \psi_0 = \psi_0 \) in eqn. (12.4.15) gives:

\[
V_R^\Psi = \pi \kappa \psi_0^2 \{1 - \coth \kappa D + \cosech \kappa D\}
\]

\[
= \pi \kappa \psi_0^2 \left[1 \pm \frac{\cosh \kappa D - 1}{\sinh \kappa D}\right] = \pi \kappa \psi_0^2 \left[1 - \frac{\exp(\kappa D) + \exp(-\kappa D) - 2}{\exp(\kappa D) - \exp(-\kappa D)}\right]
\]

\[
= \pi \kappa \psi_0^2 \left[1 - \frac{\{\exp(\kappa D/2) - \exp(-\kappa D/2)\}^2}{\exp(\kappa D) - \exp(-\kappa D)}\right]
\]

\[
= \pi \kappa \psi_0^2 \left(1 - \tanh(\kappa D/2)\right).
\]

Alternatively, from the identities:

\[\cosh p = 1 + 2 \sinh^2 p/2 \text{ and } \sinh p = 2 \sinh(p/2) \cosh(p/2)\] we have:

\[\left[\cosh \kappa D - 1\right]/\sinh \kappa D = 2 \sinh^2(p/2)[2 \sinh p/2 \cosh p/2] = \tanh p/2.\]

Exercise 12.5.1. Establish eqns (12.5.2 and 12.5.3). Also establish the identity of the alternate expressions in eqn (12.5.4).

Solution 12.5.1 \( V_R^\Psi = \pi a \int V_R \text{ (flat plate)} \, d\Omega \) eqn (12.5.1) and introducing eqn (12.3.16):
\[
V_R^\psi = \pi a \int_{H}^{\infty} \frac{2n^0 kT}{\kappa} \psi_0^2 [1 - \tanh(\kappa D/2)] dD = \frac{\pi a 2n^0 z^2 e^2}{\kappa kT} \psi_0^2 \int_{H}^{\infty} [1 - \tanh(\kappa D/2)] dD
\]

\[
= \pi a e \kappa \psi_0^2 \left[ \int_{H}^{\infty} \frac{\exp(\kappa D/2) + \exp(-\kappa D/2)}{\exp(\kappa D/2) + \exp(-\kappa D/2)} dD \right]
\]

\[
= \pi a e \kappa \psi_0^2 \int_{H}^{\infty} \frac{2\exp(-\kappa D/2) dD}{\exp(\kappa D/2) + \exp(-\kappa D/2)} = \pi a e \kappa \psi_0^2 \int_{H}^{\infty} \frac{2\exp(-\kappa D) dD}{1 + \exp(-\kappa D)}
\]

\[
= -2\pi a e \psi_0^2 \int_{H}^{\infty} \frac{d[\exp(-\kappa D)]}{1 + \exp(-\kappa D)} = -2\pi a e \psi_0^2 \left[ \ln(1 + \exp(-\kappa D)) \right]_H^\infty
\]

\[
= 2\pi a e \psi_0^2 \ln[1 + \exp(-\kappa H)] \quad \text{eqn (12.5.3) and if } s = r a \text{ and } \tau = \kappa a
\]

and \( H > r - 2a \) then \( \kappa H = \kappa [s - 2a] = \kappa a(s - 2) = \tau(s - 2) \) so that eqn (12.5.4) follows immediately.

\[
V_R^a = 2\pi a e \psi_0^2 \ln \left[ \frac{1 + \exp(-\kappa H)}{1 - \exp(-2\kappa H)} \right] = 2\pi a e \psi_0^2 \ln \left[ \frac{1 + \exp(-\kappa H)}{1 + \exp(-\kappa H)[1 - \exp(-\kappa H)]} \right]
\]

\[
= -2\pi a e \psi_0^2 \ln[1 - \exp(-\kappa H)]
\]

Exercises. 12.6.1 The condition for the potential energy barrier to just disappear is that \((V_A + V_R) = 0\) and \(d(V_A + V_R)/dD = 0\) simultaneously. Show that this occurs when \(\kappa D = 2\). Hence establish the relations (12.6.4) and (12.6.5).

12.6.2 Use the approximate expression (12.5.5) together with an appropriate attractive energy for spheres of radius \(a\) (Chapter 11) to establish the relation (12.6.7) for the c.c.c. under conditions of low surface potential.

12.6.3 Calculate the repulsive potential energy (under constant potential conditions) between two spherical particles of radius 0.5 \(\mu\)m, of surface potential 35mV, when the electrolyte concentration is (a) \(10^{-4}\) M NaCl and (b) \(10^{-2}\) M NaCl. (Use \(H\) values from 0 to 20 nm.)

S12.10

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12.6.4 Calculate the attraction potential energy between the particles in Exercise 12.6.3 (assuming that \( A = 5 \times 10^{-20} \) J) as a function of \( H \) for \( 0 < H < 20 \) nm. Combine this with the curves for \( V_r \) found in Exercise 12.6.3 to produce curves for \( V' \) and comment on the result. (Ignore \( V_s \).)

**Solutions 12.6.1**

\[
V_r = -\frac{A}{12\pi D^2} + \frac{64n^0kT}{\kappa} Z^2 \exp(-\kappa D) = 0 \quad (1)
\]

and

\[
\frac{dV_r}{dD} = \frac{2A}{12\pi D^2} - 64n^0kT Z^2 \exp(-\kappa D) = 0 \quad (2)
\]

\[
t.e. \quad \frac{A}{12\pi D^2} = \frac{64n^0kT Z^2}{\kappa} \exp(-\kappa D) = \frac{64n^0kT Z^2 D}{2} \exp(-\kappa D) \quad \text{from (1) & (2) resp.}
\]

So \( \kappa D = 2 \). Substituting this in (1) then gives: \( A \kappa^2 = 12\pi (\kappa D)^2 \), \( 64n^0(kT/\kappa)Z^2 \exp(-2) \)

\[
\frac{2n^0\varepsilon^2e^2}{\varepsilon kT} = \frac{12\pi \times 64n^0kT Z^2 \exp(-2)}{A\kappa}
\]

\[
\kappa^2 = \left[ \frac{64\times 24 \times \pi \varepsilon k^2 T^2 Z^2 \exp(-2)}{z^2e^2A} \right]^2
\]

So \( n^0 = \left[ \frac{64^2 \times 24^3 \times \pi^3 \varepsilon^3 k^3 T^3 Z^4 \exp(-4)}{2z^6e^6A^2} \right] \) ions \( m^3 \)

(c.c.c.(mol/L) = \( \frac{64^2 \times 24 \times 12 \times 10^{-3} \times \pi \varepsilon k^3 T^3 Z^4 \exp(-4)}{N_Az^6e^6A^2} \))

\[
= 64 \times 24 \times 12 \times 10^{-3} \times (4\pi\varepsilon_0)^{3/2} (kT)^3 Z^4 \exp(-4) / N_A(z\varepsilon)^{3/2} A^{3/2} \approx 0.107 \times (4\pi\varepsilon_0)^{3/2} (kT)^3 Z^4 / z^6 A^2
\]

for \( A \) in Joules.

S12.11

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12.6.2 \[ V_t = 2\pi e a \psi_0^2 \exp(-\kappa H) - Aa/12H = 0 \text{ assuming } H << a \]  
(1)

Then \[ dV_t/dH = -2\pi e a \kappa \psi_0^2 \exp(-\kappa H) + Aa/12H^2 = 0 \]
(2)

and these are simultaneously true when \( \kappa H = 1 \). Then substituting in (1):

\[
\kappa = \frac{12 \times \kappa H \times 2\pi e \psi_0^2 \exp(-1)}{A} \quad \text{or} \quad n^0 = \left[ \frac{24 \pi^2 e^2 \psi_0^4}{2z^2 e^2 A^2} \kappa \exp(-2) \right] 
\]

\[
= \left[ \frac{3.65 \times 10^{-35}}{A^2} \right] \frac{\psi_0^4}{z^2} = 22800 \frac{\psi_0^4}{z^2} \quad \text{for } A = 4 \times 10^{-20} \text{ J and } \psi_0 \text{ in volts.}
\]

For a c.c.c. of 0.05 mol L\(^{-1}\) and \( z = 1 \) this would give \( \psi_0 = 38.5 \text{ mV} \) which is reasonable.

12.6.3 \[ V_R^\Psi = 2\pi e a \psi_0^2 \ln [1 + \exp(-\kappa H)] \] from eqn (12.5.3.) For \( C = 10^{-4} \text{ M, } \kappa = 3.288 \times 10^{-2} \text{ nm}^{-1} \) from eqn (7.3.14).

\[ V_R^\Psi = 2.692 \times 10^{18} \ln[1 + \exp(-\kappa H)] \] [Note that \( \kappa a = 16 \) in this case so the Deryaguin approximation is quite good.]

<table>
<thead>
<tr>
<th>( H )</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \kappa H )</td>
<td>0</td>
<td>.0658</td>
<td>.1315</td>
<td>.1973</td>
<td>.263</td>
<td>.3288</td>
<td>.3946</td>
<td>.4603</td>
<td>.5261</td>
<td>.5918</td>
<td>.6576</td>
</tr>
<tr>
<td>( 10^{18} V_R^\Psi )</td>
<td>1.866</td>
<td>1.779</td>
<td>1.695</td>
<td>1.613</td>
<td>1.535</td>
<td>1.459</td>
<td>1.387</td>
<td>1.317</td>
<td>1.250</td>
<td>1.185</td>
<td>1.124</td>
</tr>
</tbody>
</table>

For \( C = 0.01 \text{ M, } \kappa = 0.3288 \text{ nm}^{-1} \) and then

<table>
<thead>
<tr>
<th>( H )</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \kappa H )</td>
<td>0</td>
<td>0.6576</td>
<td>1.315</td>
<td>1.973</td>
<td>2.630</td>
<td>3.288</td>
<td>3.946</td>
<td>4.603</td>
<td>5.261</td>
<td>5.918</td>
<td>6.58</td>
</tr>
<tr>
<td>( 10^{18} V_R^\Psi )</td>
<td>1.866</td>
<td>1.124</td>
<td>0.64</td>
<td>0.3505</td>
<td>0.1837</td>
<td>.0986</td>
<td>.0516</td>
<td>.0268</td>
<td>.0139</td>
<td>.00723</td>
<td>.0038</td>
</tr>
</tbody>
</table>

(\( \kappa a \) is even larger in this case (~160) so the Deryaguin approximation is well justified.)

12.6.4 We need first an approximate form for \( V_A \) for the case \( q = q = a = a \). From eqn
(11.3.15) we have \( V_A = [A_{12}a/12H][1 + 3H/4a + 2(H/a)\ln(H/a)] \). Since \((H/a)_{\text{max}} = 0.04\) we need to use only the first term.

\[
\begin{array}{cccccccccccccc}
H & 1 & 2 & 4 & 6 & 8 & 10 & 12 & 14 & 16 & 18 & 20 \\
-10^{18}V_A & 2.084 & 1.042 & 0.521 & 0.347 & 0.26 & 0.208 & 0.1736 & 0.1488 & 0.1302 & 0.116 & 0.104 \\
\end{array}
\]

\[ V_A = -5 \times 10^{-20} \times 500/12H \text{(nm)} = -2.083 \times 10^{-18}/H \]

For \( C = 10^{-4} \) M

\[
\begin{array}{cccccccccccccc}
H & 0 & 2 & 4 & 6 & 8 & 10 & 12 & 14 & 16 & 18 & 20 \\
10^{18}V_A^H & \infty & 0.737 & 1.174 & 1.266 & 1.275 & 1.251 & 1.213 & 1.168 & 1.120 & 1.069 & 1.02 \\
\end{array}
\]

For \( C = 0.01 \) M

\[
\begin{array}{cccccccccccccc}
H \text{(nm)} & 0 & 2 & 4 & 6 & 8 & 10 & 12 & 14 & 16 & 18 & 20 \\
10^{18}V_A^H & \infty & 0.82 & 0.119 & 0.035 & 0.073 & 0.109 & 0.122 & 0.122 & 0.116 & 0.108 & 0.10 \\
\end{array}
\]

\( A = 5 \times 10^{-20} J = 12 kT \) (for \( T = 300 \) K). The c.c.c. must be a little more than \( 10^2 \) M. Note the development of a secondary minimum for \( c = 0.01 \) M in the region around \( H = 10 \) nm. The depth is about \( 30 kT \), which is very significant in this case. (Note that a particle of density 3 g/cm\(^3\) and 0.5 \( \mu \)m radius has a gravitational energy of 30 \( kT \) in water when raised a height of 12 \( \mu \)m above the base level.)
Chapter 12
Solutions (contd.)

Exercises 12.8.1 Show that eqn (12.8.4) is a solution of eqn (12.8.3) with the boundary conditions \( v = v_0, \quad r = \infty \). Establish eqn (12.8.5), assuming \( v = 0 \) for \( r \approx R = 2a \) (i.e. the approaching particle is assumed to be swallowed up on contact).

12.8.2 Use the Einstein-Smoluchowski eqn (1.5.25) to show that the mutual diffusion coefficient of individual particles is \( 2D_v \) (Hint: consider the average value of \( (x_1 - x_2)^2 \) where \( (x_1 - x_2) \) is the relative displacement and note that \( \langle x_1 x_2 \rangle = 0 \). Establish eqn (12.8.6) assuming that in the early stages of coagulation the rate is the same as the collision frequency. (Why is the \( \frac{1}{2} \) included?)

12.8.3 Establish eqn (12.8.7) by integrating eqn (12.8.6) with \( v_0 \) treated as a variable.

12.8.4 Establish equations (12.8.13) and (12.8.14).

12.8.5 Establish equations (12.8.17) and (12.8.18). (Hint: Estimate the mutual diffusion coefficient for the two aggregates, using Smoluchowski’s approximation \( D_v R = 4D_c a \).)

12.8.6 Consider a particle of mass \( m \) travelling with velocity \( \mathbf{v} \) in a fluid. Newton’s law gives \( -m\mathbf{a} = \mathbf{F} \) so that \( \mathbf{v} = \mathbf{v}_0 \exp(-Bt/m) \) where \( B \) is the coefficient of frictional resistance (cf. Exercise 3.1.1). Show that if the particle starts with a kinetic energy of \( \rho_v kT \) then it will come to rest after travelling a distance of the order of \( (2\rho_v kT)^{1/2}/B \). Use reasonable values for these quantities to show that a colloidal particle of initial energy \( 10kT \) will come to rest in water after travelling at most only a fraction of a nanometre.

12.8.7 Consider the differential equation (12.8.22) under steady-state conditions:

\[
\frac{J}{8\pi D} = r^2 \frac{dv}{dr} + \frac{vr^2 d\nu}{kT dr} = \text{a constant.}
\]

Show, using the differential \( d[\exp(V/kT)\nu] \) that the solution is given by eqn (12.8.23) for the boundary conditions \( V = 0, \quad v = v_0 \) at \( r = \infty \).

12.8.8 Overbeek (1952) gives as an approximation for \( W \) the expression:

\[
W \approx [1/2\kappa_1] \exp [V_{\text{max}} kT].
\]

Estimate \( W \) from this relation for the data in Fig. 12.8.4 and compare it with the exact result.

12.8.9 Derive the relation between the effective density of an aggregate and its fractal dimension, taking account of buoyancy. For particles of radius 250 nm, calculate \( a_e \phi_s \) and \( \rho_E \) for aggregates of 2000 particles in aqueous suspension with the following fractal dimensions: 1.7, 2.0, and 2.5.

(2.14)
Solutions 12.8.1 \( J_f = D_4 \pi r^2 \frac{\partial v}{\partial r} \) \hspace{1cm} (1)

If \( v = v_0 - J_f / [D_4 \pi r] \) \hspace{1cm} (2) then \( \partial v / \partial r = J_f / D_4 \pi r^2 \) which satisfies (1) and also, from (2), \( v = v_0 \) for \( r \to \infty \). For \( r = 2a \) we have \( 0 = v_0 - J_f/\pi \). \( J_f = 8\pi Da v_0 \).

12.8.2 \( <x^2> = 2Dt \) \hspace{1cm} (Einstein - Smoluchowski equation)

Now \( <(x_1 - x_2)^2> = <x_1^2 - 2x_1 x_2 + x_2^2> = \sum x_i^2/n - 2\sum x_i x_j/n + \sum x_j^2/n \)

\( = x_1^2 + x_2^2 \) \hspace{1cm} if \( x_1 x_2 \). \hspace{1cm} (This last eqn. follows from the fact that \( x_1 \) and \( x_2 \) are as likely to be negative as positive.)

Then \( <x_1^2> + <x_2^2> = 2D_1 t + 2D_2 t = 2(D_1 + D_2) t = 2D_\tau t \) and so \( D_{12} = D_1 + D_2 = 2D_\tau \).

\( J_f \) is the number of collisions with the central particle and so the total number of collisions which occur is proportional to \( J_f \times v_0 \) since each particle can act as the central particle.

But this counts every particle twice (once as the central particle and once as a particle colliding with it) so the actual rate of decrease of particles is half that, i.e.

\[ -\frac{dv}{dt} = \frac{1}{2} \times J_f \times v_0 \]

12.8.3 From eqn (12.8.6) with \( R_{11} = 2a \) we have: \( -[dv/v^2] = [8\pi D_\tau]/t \) so \( v^{-1} = 8\pi D_\tau t + C \) and since \( v = v_0 \) at \( t = 0 \), \( C = v_0^{-1} \).

\[ 1/v - 1/v_0 = 8\pi D_\tau t \]

\( \tau \) is the time for \( v \) to fall from \( v_0 \) to \( v_0/2 \) so

\[ 2/v_0 - 1/v_0 = 8\pi D_\tau \tau \] and, hence, \( \tau = 1/[8\pi D_\tau v_0] \).

12.8.4 From eqn (12.8.11) introducing the Smoluchowski approximation \( (D_\rho R_\rho = 4D_\rho \rho) \):

\[ \frac{dv_k}{dt} = \frac{1}{2} \times 4\pi \times 4D_1 a \left[ \sum_{i=1}^{j=k-1} v_i v_j - 2v_k \sum_{i=1}^{j=k} v_i \right] = 8\pi D_1 \rho [x] \]

Therefore \[ \frac{d}{dt} \sum_{k=1}^{M} v_k = -8\pi D_1 \rho \left[ \sum_{i=1}^{M} \sum_{j=1}^{M} v_i v_j - 2\sum_{i=1}^{M} \sum_{k=1}^{M} v_i v_k \right] = -8\pi D_1 \rho \sum_{i=1}^{M} \sum_{k=1}^{M} v_i v_j \]

\[ = -8\pi D_1 \rho \left( \sum_{i=1}^{M} v_i \right)^2 \]

That is \( dv_\tau /dt = -8\pi D_1 a v_\tau^2 = -k_1 v_\tau^2 \) and integrating as before:

\[ \tau = 1/2 \rho \]

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\[1/v_T - 1/v_0 = 8 \pi D \alpha t \text{ and hence } v_T = v_0 \left[1 + 8 \pi D \alpha v_0 \right] = v_0 / (1 + t/\tau)\]

12.8.5

\[J_s = \frac{R_y}{R_x} \int_{-R_x}^{R_y} \frac{2z}{d} \sqrt{R_y^2 - z^2} \, dz = 2 \int_{0}^{R_y} v G \sqrt{R_y^2 - z^2} \, dz\]

\[= \left[ \frac{2}{3} v G R_y \left( R_y^2 - z^2 \right)^{3/2} \right] \text{ from } z = 0 \text{ to } z = R_y\]

\[= 4v \, G \, R_y^{3/2}.\]

Now from eqn (12.8.5) \(J_B = 4 \pi D_2 \alpha v_0\) where \(D\) is the mutual diffusion coeff. = 2\(D_1\).

Therefore \(J_B = 16 \pi D_1 \alpha v_0\) and

\[J_B/J_B = (4/3) \pi R_y^2 \left[ (16 \pi D_1 \alpha v_0) = GR_y^3 / 12 \pi D_1 \alpha \right]\]

and using (1.5.18 & 19) \(J_B/J_B = GR_y^3 \eta / 2kT\) which is eqn (12.8.18).

12.8.6 \(v = v_0 \exp(\beta t/m)\) with \(v_0 = [p_k / (kT/m)]^{1/2}\) and \(S = \int \nu \, dt = \int v_0 \exp \left[ -\beta t/m \right] \, dt\)

\[S = \left[ \left( \frac{v_0 m}{\beta} \exp \left[ \frac{\beta t}{m} \right] \right) \right] = \frac{v_0 m}{\beta} - \frac{v_0 m}{\beta} \exp \left[ \frac{\beta t}{m} \right]\]

As \(t \to \infty\), \(S - v_0 m / B = [2p_k \eta / (kT)]^{1/2} B\). Using \(r = 10^{-6} \text{ m}\) and \(\rho = 1 \text{ kg/m}^3 \eta = 10^{-3} \text{ Pa s}\):

\[S = \left[ 20 \times 1.38 \times 10^{-23} \times 300 \times (4/3) \pi \times (10^{-6})^3 \times 10^{-3} \right] / (6 \pi \times 10^{-6} \times 10^{-3}) = 1 \text{ nm}\]

12.8.7 Consider the differential equation:

\[\frac{J}{8 \pi D} = \rho r^2 \frac{\partial \nu}{\partial r} + \frac{\nu r^2}{kT} \frac{\partial V}{\partial r} = \text{constant} \ (1)\]

(Both \(V\) and \(\nu\) are functions of \(r\) only.)

\[\frac{d}{dr} \left[ v \exp \left( \frac{V}{kT} \right) \right] = \nu \frac{1}{kT} \exp \left[ \frac{V}{kT} \right] \frac{dV}{dr} + \exp \left[ \frac{V}{kT} \right] \frac{dv}{dr} \ (2)\]

\(12 \cdot 16\)

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From (1):

\[
\frac{dv}{dr} + \frac{v}{kT} \frac{dV}{dr} = \frac{C}{r^2}
\]  
(3)

Multiplying by \(\exp[V/kT]\):

\[
\exp[V/kT] \frac{dv}{dr} + \frac{v}{kT} \exp[V/kT] \frac{dV}{dr} = \frac{C \exp(V/kT)}{r^2}
\]  
(4)

But from (2)

\[
\int_{v=v_0}^{v'=0} d[v \exp(V/kT)] = \int_{r} \frac{C \exp(V/kT) dr}{r^2}
\]  
(5)

\[
v \exp[V/kT] - v_0 = C \int_{r} \frac{\exp(V/kT) dr}{r^2}
\]  
(6)

\[-v_0 = C \int_{2a} \frac{\exp(V/kT) dr}{r^2}
\]  
(7)

\[
C = \frac{v_0}{\int_{2a} \frac{\exp(V/kT) dr}{r^2}} = \frac{J}{8 \pi D}
\]  
(8)

From (6):

\[
v = v_0 \exp[-V/kT] + \frac{J}{8 \pi D} \exp[-V/kT] \int_{2a} \frac{\exp(V/kT) dr}{r^2}
\]

which is eqn (12.8.23).

12.8.8. \(W = [1/2 \kappa a] \exp[V_{\text{max}}/kT] = [2 \times 10^6 \times 10^{-5}]^{-1} \exp(15) = e^{15}/20 = 1.6 \times 10^4\).

This is out by a factor of 3 but is not a bad approximation.
12.8.9 The effective density \( \rho_E = \rho_A - \rho_L = \phi_b \left( \rho_S - \rho_L \right) \) where \( \phi_b \) is the volume fraction of solid in the aggregate.

But \( \phi_b = \left[ \frac{a_s}{a_s + a_L} \right]^3 \) from eqn (12.8.30) = \( \left[ \frac{a_k}{a_s + a_L} \right]^3 \) from eqn (12.8.31) = \( \left[ \frac{a_k}{a_s} \right] \theta^{-3} \).

So \( \rho_E = \left[ \frac{a_k}{a_s} \right] \theta^{-3} (\rho_S - \rho_L) = B \theta^{-3} \) where \( d_r = 3 - y \) and \( B = (\rho_S - \rho_L) / a_1 \theta^{-3} \).

For \( a_1 = 250 \text{ nm} \), \( k = 2000 \) and \( \rho_S - \rho_L = 1 \text{ g cm}^{-3} \) we have

<table>
<thead>
<tr>
<th>( d_r )</th>
<th>1/( d_r )</th>
<th>( k^{1/4} )</th>
<th>( a_k - a_L^{1/4} )</th>
<th>( \theta_b = \left( k^{1/4} \right)^{-3} )</th>
<th>( \rho_E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>0.588</td>
<td>87.3</td>
<td>175 ( \mu )m</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>2.0</td>
<td>0.5</td>
<td>44.72</td>
<td>11.18 ( \mu )m</td>
<td>0.0224</td>
<td>0.0224</td>
</tr>
<tr>
<td>2.5</td>
<td>0.4</td>
<td>20.91</td>
<td>5.228</td>
<td>0.219</td>
<td>0.219</td>
</tr>
</tbody>
</table>

**Exercises**

12.9.1 Use the van der Waals equation of state [eqn (11.1.1)] to show that the Boyle temperature, \( T_B \) is given to good approximation by \( T_B = a/bR \).

12.9.2 Show that for a gas obeying the van der Waals equation (11.1.1):

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[ \frac{\partial U}{\partial V} \right]_T + P = \frac{R}{(V_m - b)}
\]

Hence compare the entropy change involved in an isothermal expansion with that occurring for an ideal gas. [This is the change in configurational entropy.] \( V_m \) is the molar volume.

**Solutions**

12.9.1 \( (P + a/\bar{\nu}) (\bar{\nu} - b) = RT \) \hspace{1cm} (1) \hspace{1cm} and \( P \bar{\nu} = RT_B \) \hspace{1cm} (2).

From (1) \( P \bar{\nu} + a/\bar{\nu} - Pb = ab/\bar{\nu}^2 = RT \).

Substituting from (2) : \( a/\bar{\nu} - b/RT_B \bar{\nu} = ab/\bar{\nu}^2 = 0 \) and neglecting the last term (as the product of two small terms) we get : \( a = bRT_B \) so \( T_B = a/Rb \).

12.9.2 \( dU = T \bar{\nu} dS - pdV \). So \( (\partial U/\partial V)_T = T(\partial S/\partial V)_T - p \) or \( (\partial S/\partial V)_T = T^{-1} \left[ (\partial U/\partial V)_T + p \right] \).

But \( dF = -SdT - pdV \) (Eqn A5.3 for one component).

So by cross differentiation: \( (\partial S/\partial V)_T = (\partial F/\partial T)_V \).

For a gas obeying the van der Waals equation:

\[
\frac{1}{2}
\]
\[
\left(\frac{\partial p}{\partial T}\right)_v = \left[ \frac{\partial}{\partial T}\left( \frac{RT}{v-b} - \frac{a}{v^2} \right) \right]_v = \frac{R}{v-b}
\]

So for an isothermal expansion:

\[
\Delta S = \int_{V_1}^{V_2} \left( \frac{\partial S}{\partial V} \right)_T \, dV = nR \int_{V_1}^{V_2} \frac{dV}{V - nb} = nR \ln \frac{V_2 - nb}{V_1 - nb}
\]

for a system containing \( n \) moles.

This should be compared with the corresponding expression for an ideal gas: \( \Delta S = nR \ln \frac{V_2}{V_1} \).

It is obvious that finite volume parameter, \( b \) has a dominant effect on the entropy change when \( V_1 \) or \( V_2 \) become small enough.
Solutions
Chapter 13

Exercises. 13.2.1 The de Broglie wavelength for translational motion of a molecule was defined as \( \lambda = \hbar/(mkT)^{1/2} \). What is the corresponding translational velocity of the molecules? What is the kinetic energy (in terms of \( kT \))? 

13.2.2 Verify that the depth of the energy minimum in Fig. 13.2.1 is \( \epsilon \) where \( \epsilon \) is defined in eqn (13.2.2). Where is the minimum, relative to \( \delta \)? Plot the function \( u(r) \) for \( 0 \leq r \leq 1 \) nm using \( \delta = 0.3 \) nm, \( \epsilon = 2kT \).

Solutions:

13.2.1 de Broglie wavelength for the translational motion \( \lambda = h/(mkT)^{1/2} \). The corresponding translational velocity \( (v) \) is derived from \( \lambda = h/p = hv/mv \), i.e. \( v = h/m\lambda = h(mkT)^{1/2}/mv \). The translational kinetic energy \( \frac{1}{2}mv^2 = kT/2 \).

13.2.2

\[
\begin{align*}
\frac{da(r)}{dr} &= 4\epsilon \left[ \frac{12}{r} \left( \frac{\delta}{r} \right)^{12} + 6 \left( \frac{\delta}{r} \right)^{6} \right] = 0 \quad \text{when} \quad 2(\delta/r)^6 = 1
\end{align*}
\]

i.e. \( r = 2^{1/6}\delta \). Then \( u(r = 2^{1/6}\delta) = 4\epsilon[2^{-2} - 2^{-1}] = 4\epsilon(-1/4) = -\epsilon \)

So the minimum occurs at \( r = 2^{1/6}\delta = 1.122\delta \).

Exercises. 13.3.1 Departures from ideal behaviour in gases can be represented by a virial expansion, as for example:

\[
p = \frac{RT}{V_m} \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots \right)
\]
where \( B, C \) are the second and third virial coefficients, which are functions only of the temperature. Show that if the van der Waals equation (see exercise (12.9.1) is written as a virial expansion then \( B = (b - a/RT) \) i.e. the second virial coefficient incorporates both the attractive and repulsive components of the departure from ideal behaviour.

13.3.2 (a) Use eqn (7.11.7) for \( \psi_i \) to establish eqn (13.3.8).

(b) The number density of ions of type \( j \) at \( r \), given there is an ion of type \( i \) at the origin is \( n_j(r) = n_j g_{ij}(r) \) where \( n_j \) is the average number density of ions of type \( j \) in the system. The excess density of ions of type \( j \) is then \( \Delta n_j(r) = n_j(r) - n_j = n_j [g_{ij}(r) - 1] \). Therefore, the number of excess \( j \) ions in a spherical shell of radius \( r \) and thickness \( dr \) centred on ion \( i \) is:

\[
\Delta n_j(r) \, 4\pi r^2 dr = F(r) dr.
\]

Show that \( F(r) \) is a maximum at \( r = 1/\kappa \).

---

Solutions

13.3.1

\[
\left( p - \frac{a}{V_m^n} \right) \left( V_m - b \right) = RT
\]

\[
p = \frac{RT}{V_m^n} + \frac{bp}{V_m^n} - \frac{a}{V_m^n} + \frac{ab}{V_m^n}
\]

\[
= \frac{RT}{V_m^n} \left[ 1 + \frac{bp}{RT} - \frac{a}{RT V_m^n} + \frac{ab}{RT V_m^n} \right]
\]

\[
p = \frac{RT}{V_m^n} \left[ 1 + \frac{b}{V_m^n} \left( \frac{p V_m^n}{RT} \right) - \frac{a}{RT V_m^n} + \frac{ab}{RT V_m^n} \right]
\]

\[
= \frac{RT}{V_m^n} \left[ 1 + \left( \frac{b}{RT} \right) \frac{1}{V_m} + \frac{ab}{RT V_m^n} \right]
\]

since \( p V_m^n = RT \). So \( B - b - a/RT \) and \( C - ab/RT \) and \( D = 0 \).
13.3.2. \( g_d = \exp(-z_j e \psi_i(r)/kT) = 1 - z_j e \psi_i(r)/kT. \)

From eqn 7.11.7 with \( Q_p - z e \) for the ion:

\[
g_d = 1 - \frac{z e}{kT} \left[ \frac{1}{4 \pi \epsilon_0 \epsilon_1} \frac{z e}{r} \exp(-\kappa(r - \delta)) \right]
= 1 - \frac{z e^2}{4 \pi \epsilon_0} \left[ \frac{\exp(-\kappa(r - \delta))}{\epsilon_1 kT} (1 + \kappa \delta) r \right]
\]

(b) \( F(r) dr = \Delta n_f(r) 4 \pi r^2 dr = n_f g_d(r) - 1 \) 4πr² dr.

\[
F(r) = -4 \pi r^2 \Delta n_f \frac{z e^2}{4 \pi \epsilon_0} \left[ \frac{\exp(-\kappa(r - \delta))}{\epsilon_1 kT} (1 + \kappa \delta) r \right]
= -A \exp(-\kappa(r - \delta)) + A \kappa \exp(-\kappa(r - \delta)) = 0 \text{ when } A + A \kappa r = 0 \text{ or } \kappa r = 1.
\]

Exercise 13.4.1 Establish eqn (13.4.7).

Solution

13.4.1 \( \ln g(|r_1 - r_2|) = -W(|r_1 - r_2|)/kT \) from 13.4.2

\[
kT \frac{d}{dx_1} \ln g(|r_1 - r_2|) = - \frac{d}{dx_1} W(|r_1 - r_2|)
= - \frac{d}{dx_1} (r_1 - r_2) + \int \frac{d\omega(r_1 - r_2)}{dx_1} \rho \Phi(r_2, r_1, r_2) dr_3
\]

from 13.4.5, from which eqn 13.4.7 follows if \( g(r_1, r_2) = g(r) = g(|r_1 - r_2|) \) and this would seem to require independence of the probabilities (cf. eqn. 13.4.10).

Exercises. 13.6.1 Equation (13.6.4) has a rigorous derivation based on statistical mechanics. Here we consider a simplified heuristic derivation. The local density at \( r \) in an external field \( v(r) \)

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can be written as
\[ \rho(r) = \rho \exp \left( -\frac{W(r)}{kT} \right) \]
where \( W(r) \) is the free energy [relative to a point where \( v(r) = 0 \)] of putting a molecule at \( r \). The quantity \( W(r) \) has two contributions: (a) the direct interaction between the molecule and the external field, i.e. \( v(r) \) and (b) the effect which the presence of a molecule at \( r \) will have on the local density of molecules around \( r \). The resulting excess of molecules (which may be positive or negative) due to (b) also interacts with the external field and contributes to \( W(r) \). For a weak external field this second contribution has the form
\[ \int \left[ \rho g(r - r') - \rho \right] v(r') \, dr' \]
where \([\rho g(r - r') - \rho] \, dr'\) is the excess number of molecules at the volume element \( dr' \) located at \( r' \) given that there is a molecule at \( r \).

Start with the above argument and derive eqn (13.6.4) assuming that \( v/kT << 1 \).

13.6.2 Obtain (13.6.5) using the three dimensional convolution theorem (Appendix A4). (The symbol \( \sim \) above a function denotes its Fourier transform).

13.6.3 Derive eqn (13.6.6).

Hints: \[ \int f(r) \, dr = \int_0^{2\pi} \int_0^\pi \int_0^\infty r^2 f(r) \, d\phi \, d\theta \, r^2 \, dr \]
\[ \exp(-ik \cdot r) = \exp(-ikr \cos \theta) \quad \text{and} \quad \sin x = \frac{1}{2i} [\exp(ix) - \exp(-ix)] \]

**Solutions**

13.6.1 \[ \rho(r) = \rho \exp \left( -\frac{W(r)}{kT} \right) = \rho \left[ 1 - \frac{W(r)}{kT} \right] \]
assuming \( W(r) \leq kT \) since \( W(r) = v(r) \)
\[ \rho \left[ 1 - \frac{W(r)}{kT} \right] = \rho \left[ 1 - \frac{v(r)}{kT} \right] \]
\[ \rho \left[ 1 - \frac{v(r)}{kT} \right] = \rho \left[ 1 - \frac{v(r)}{kT} \right] \]
\[ \rho \left[ 1 - \frac{v(r)}{kT} \right] = \rho \left[ 1 - \frac{v(r)}{kT} \right] \]

13.6.2 From eqn (13.6.4):

\[ 1 \partial \cdot \text{a} \]
\[- \frac{kT}{\rho^2} [\Delta \rho(r) + \rho \frac{\nabla r}{kT}] = f(r) = \int h(r-r') v(r') \, dr' \]

But if \( f(r) = \int h(r-R) v(R) \, dR \) \((A4.8)\) then \( \tilde{f}(Q) = \tilde{h}(Q) \tilde{v}(Q) \) \((A4.9)\).

\[ \Delta \tilde{\rho}(Q) + \frac{\rho}{kT} \tilde{v}(Q) = -\frac{\rho^2}{kT} \tilde{h}(Q) \tilde{v}(Q) \]

\[ \Delta \tilde{\rho}(Q) = -\frac{\rho}{kT} [1 + \rho \tilde{h}(Q)] \tilde{v}(Q) \]

which is \((13.6.5)\).

13.6.3

From eqn \((A4.5)\) \( \tilde{h}(Q) = \int \exp(-i Q r) h(r) \, dr = \int \exp(-i Q r \cos \theta) h(r) \, dr \) (hint2)

\[ = \frac{2}{\pi} \int_{0}^{\pi} \int_{0}^{\pi} \sin \theta r^2 \exp(-i Q r \cos \theta) \, d\theta \, dr \] (hint1)

\[ = 2\pi \int_{0}^{\pi} \int_{0}^{\pi} \exp(-i Q r \cos \theta) r \exp(i Q r) \, dr \, d\theta \]

\[ = 2\pi \int_{0}^{\pi} \int_{0}^{\pi} \exp(-i Q r \cos \theta) r \cos \theta \, dr \, d\theta \] (hint3)

But \( \tilde{\chi} = -\frac{\rho}{kT} [1 + \rho \tilde{h}(Q)] = -\frac{\rho}{kT} [1 + \frac{4\pi}{Q} \int_{0}^{\pi} \sin \theta r \, dr] \).

Exercises. 13.7.1 Justify the final form for \( I_\chi \) in eqn (13.7.4) from the previous equation.

13.7.2 Compare the time scale of molecular motion with the time taken for light to pass through a scattering cell.

13.7.3 Show that \( F(Q, t=0) = S(Q) \) using eqn (13.7.11).
Solutions

13.7.1 The first term (1) corresponds to the term \( i = j \) in the series and gives \( \exp(0) = 1 \) for each of the \( N \) terms that occurs. The second term then collects the remaining terms leaving out the \( i = j \).

13.7.2 Molecular motions occur on a time scale \( t \sim \alpha v \) where \( \alpha = \) atomic radius and \( v = \) velocity = \( \sqrt{(2kT/m)} = \sqrt{(kT/m)} \). Compare this with the time for light to cover say \( 10^3 \alpha \) which is \( 10^3 \alpha c \). The ratio of the times is \( [mc^2/10^6kT]^{1/2} \) which is about 130.

13.7.3 \[
F(Q, t = 0) = 1 + \int dr \exp[-iQ.r] [G(r, 0) - \rho] \\
= 1 + \int dr \exp[-iQ.r] [\rho g(r) - \rho] \quad \text{from [13.5.2]} \\
= 1 + \rho \int dr \exp[-iQ.r] \rho g(r) dr = 1 + \rho \mathcal{R}(Q) \quad \text{from (A4.5)} \\
= S(Q) \quad \text{(from eqn. 13.7.7)}.
\]

Exercises. 13.8.1 Verify eqn (13.8.6).

13.8.2 Why is it not possible to use the energy equation to obtain the thermodynamics of a hard sphere fluid?

13.8.3 Plot the functions \( \rho^\delta pkT \) and \( \rho^\beta pkT \) for \( 0 < \Phi \leq 0.5 \) and compare them with the Carnahan and Starling eqn (13.8.10) which represents the hard sphere fluid very well.

Solutions

13.8.1 \( g(r) = \exp(-u(r)/kT) + h(r) = c(r) = 1 - [u(r)/kT] + h(r) - c(r) \).

But \( g(r) = 1 + h(r) \) so \( c(r) = -u(r)/kT \).

13.8.2 Because \( u(r) = 0 \) for all \( r > \delta \) and \( g(r) = 0 \) for \( r < \delta \) so that the integral in eqn. (13.6.2) is zero everywhere (except for a delta function on contact). Only the kinetic energy term remains and the unknown value of the integral of the delta function.

13.8.3 Plots of functions 13.8.8, 13.8.9 and 13.8.10 are given in the figure below.

13.8.6
Solutions

Chapter 14


14.1.2 Consider three latex particles interacting through a screened Coulomb pair potential \( U = \exp(-r_{ij}/\lambda d)/r_{ij} \), where \( r_{ij} \) is the distance between particles i and j. Fix two of the particles, and let the third move on a locus at any fixed distance measured from the midpoint of the first two. Show that the sum of the pair potentials is a minimum when the centres of the three particles form an isosceles triangle, and is a maximum when the particles are collinear.

14.1.3 Use the equipartition theorem to estimate the average thermal velocity, \( v \) (m/s), of particles moving in a given direction in a dispersion in terms of their mass, \( m \) (kg) and the temperature, \( T \) (K).

14.1.4 Use the previous result to find the time taken by a polystyrene sphere of diameter 234 nm to travel 1 diameter in a suspension at \( T = 298 \) K, assuming it moves in a straight line. (Take the density of polystyrene to be 950 kg/m³.) Now calculate the time the particle takes to travel 5.3 \( \mu \)m, assuming it takes a random walk with step-length equal to: (a) the diameter; and (b) \( \frac{1}{4} \) diameter. Discuss your answers with reference to the time-scales which occur in simple liquids, and compare them with those observed in the experiments of Clark et al. (1983), to which these numerical values correspond.

Solutions

14.1.1 \( \kappa_T = \chi_T = p^{-1}(\partial \rho/\partial p)_T \) and \( p = 1/d^3 \) so \( \partial \rho = -3d^{-4} \partial d = -3p \partial \ln d \)

so \( \partial \ln d = -3d \partial \ln d \) and \( \kappa_T = (\partial \ln \rho/\partial p)_T = -3(\partial \ln d/\partial p)_T \).

14.1.2 The centres of the three particles define a plane. The locus of particle 3 is a sphere of radius \( d \) centred on the midpoint of the line joining 1 and 2. We need only to solve the problem for the particle 3 in the plane of the paper.

Distance from 1 to 3 is \( \sqrt{d^2 \sin^2 \theta + (d \cos \theta + r)^2} = r_{13} \)

Distance from 3 to 2 is \( \sqrt{d^2 \sin^2 \theta + (d \cos \theta - r)^2} = r_{23} \)

We must show that:

\[
U = \frac{\exp(-\kappa r)}{r} + \frac{\exp(-\kappa r_{13})}{r_{13}} + \frac{\exp(-\kappa r_{23})}{r_{23}}
\]

is a minimum when \( \theta = \pi/2 \) and a maximum when \( \theta = 0 \). Since \( r \) and \( d \) are constant the

\[\text{\textbf{14.1.2}}\]
minimum in \( U \) will occur when the function \( f(0) = \left[ \exp(-\kappa r_{13})/r_{13} \right] + \left[ \exp(-\kappa r_{23})/r_{23} \right] \) is a minimum.

\[
\frac{df(0)}{d\theta} = -\left[ \frac{\kappa \exp(-\kappa r_{13})}{r_{13}} + \frac{\exp(-\kappa r_{13})}{r_{13}^2} \right] \frac{dr_{13}}{d\theta} - \left[ \frac{\kappa \exp(-\kappa r_{23})}{r_{23}} + \frac{\exp(-\kappa r_{23})}{r_{23}^2} \right] \frac{dr_{23}}{d\theta}
\]

But \( \frac{dr_{13}}{d\theta} = \sqrt{2d^2 \sin^2 \theta + (d \cos \theta + r)^2} \) \( \frac{1}{2} \left[ 2d^2 \sin \theta \cos \theta + 2(d \cos \theta + r)(-d \sin \theta) \right] \)

\[= -r (r_{13}) d \sin \theta \quad \text{and similarly} \quad \frac{dr_{23}}{d\theta} = (r d r_{23}) \sin \theta. \]

So \( \frac{df(0)}{d\theta} = 0 \) when

\[
\frac{\exp(-\kappa r_{13})}{r_{13}^2} \left( \frac{\kappa}{r_{13}} + 1 \right) rd \sin \theta - \frac{\exp(-\kappa r_{23})}{r_{23}^2} \left( \frac{\kappa}{r_{23}} + 1 \right) rd \sin \theta = 0
\]

which is obviously so when \( r_{13} = r_{23} \). So the point 3 is at the apex of an isosceles triangle and \( \theta = \pi/2 \) for the minimum and \( \theta = 0 \) for the maximum values of the function \( f \). The interaction is a maximum when \( r_{13} = r_{23} = r \) (i.e. when the point 3 is half way between 1 and 2) and a minimum when 3 is displaced from the line joining 1 and 2 but on the perpendicular bisector (for any given value of \( d \)).

14.1.3 Average thermal energy in a given direction = \( \frac{1}{2} kT = \frac{1}{2} m \bar{v}_x^2 \) so \( \bar{v}_x = \sqrt{kT/m} \)

14.1.4 For a sphere with \( d = 234 \) nm and \( \rho = 950 \) kg m\(^{-3}\); \( m = 4\pi r^3 \rho/3 = \pi d^3 \rho/6 \).

\( \bar{v}_x = \left( 1.38 \times 10^{-23} \times 298 \times 6 \times (4\pi \times (234 \times 10^{-9})^3 \times 950) \right)^{1/2} \text{ m s}^{-1} = 0.0254 \text{ m s}^{-1} \). Time taken to travel through one diameter = 234 \times 10^{-9} \times 0.025 = 9.36 \mu s.

To calculate the time taken to travel 5.3 \( \mu \)m by diffusion with a step length equal to the diameter, \( d \), we need to estimate the diffusion constant.

Now, from eqn (1.5.22):

\[ D = \frac{l^2}{2\tau} \text{ where } l \text{ is the step length and } \tau \text{ the time for each step. So } l = d \text{ and } \tau = d/l \bar{v}_x. \] Then \( D = d^2 \bar{v}_x/2d = \bar{v}_s d/2 \).

\[ D = 0.025 \times 234 \times 10^{-9}/2. \]

But the diffusion distance is given by eqn (1.5.25):

\[ <x^2>^{1/2} = 5.3 \times 10^{-9} = (2 \times 0.025 \times 234 \times 10^{-9}\times \bar{v}_x/2)^{1/2} \text{ so } \tau = 4.8 \times 10^{-9} \text{ sec. If the step length is } d/4 \text{ then } \tau = d/4 \bar{v}_x \text{ and } \]

14.2

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\( D = \frac{dV}{8} \) so \( D \) is 4 times smaller so \( t \) is 4 times longer = \( 1.9 \times 10^{-2} \) sec.

The actual step length is much smaller than \( d/4 \) so the diffusion coefficient is smaller than that calculated and the time taken to diffuse through 5.3 \( \mu \)m is much longer. Using eqns. (1.5.18 and 19) to estimate \( D \) gives \( t = 6.74 \) sec. All of these times are much more readily observed time scales compared to the time taken for a molecule of liquid to diffuse through its own diameter which is of order \( t = \frac{d^2}{2D} \) = \( (3\pi d^4/2kT) = 10^{-12} \) sec.

The time taken for the sphere of diameter 234 \( \mu \)m to diffuse through its own diameter can be calculated from its diffusion coefficient (given by eqns. 1.5.18 & 19) by using eqn 1.5.25.

\[
(\tau)^{1/3} = 2D \tau^{1/6} \quad \text{so} \quad \tau = 3\pi d^4/2kT \approx 0.013 \text{ s} \text{ or 13 ms.}
\]

Note that this is comparable with the sampling speed in the Clark experiment so by taking samples at times longer than this (~30 ms) the structure is averaged out but it reappears if one samples on a much shorter time scale.

**Exercises.** 14.2.1 Why must van der Waals attraction always dominate screened Coulomb repulsion at sufficiently large distances? Is this still the case for a bare (unscreened) Coulomb potential? At large enough distances, both potentials may be very small compared with \( kT \), in which case the question is of little or no significance; can you give an example of a system where it matters in practice?

14.2.2 F. Zernike was awarded the Nobel Prize in Physics in 1953 for the invention of phase-contrast microscopy, but is probably better known for his contribution to liquid state physics. The Ornstein - Zernike eqn was published in 1914, but not solved for any liquid until 1962. The original paper, which is reprinted in Frisch and Lebowitz (1964), was published, inter alia, to correct some misconceptions which Einstein had about correlations in the liquid state! Look it up, and compare the original derivation with that outlined in Section 13.8.

14.2.3 Show that equation (14.2.6) is identical to the repulsion energy calculated by Verwey and Overbeek (1948) for approaching spheres in the low potential approximation.

14.2.4 Derive eqn (14.2.10) from eqns (14.1.2) and (14.2.9).

14.2.5 Find expressions for \( \gamma \) (equivalent to eqn (14.2.12)) when the inter-particle potential is expressed in terms of (a) the surface potential or (b) the surface charge density, rather than the total charge.

14.2.6 Use eqns (14.2.10), (14.2.11a), and (14.2.13) to show that eqn (14.2.16) is implied by eqn (14.2.15) when the coupling, \( \Gamma \), is held fixed.

**Solutions**

14.2.1 Because the screened Coulomb potential decreases as \( \exp(-kr)/r \) and the van der

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Waals as \( r^{-n} \). The negative exponent will always decrease faster than any negative power.

In colloidal systems with particle size \( \approx 1 \mu m \) or so the van der Waals force is evident at long range (the secondary minimum).

14.2.2 No solution

14.2.3 The solution given by Verwey and Overbeek for approaching spheres at low potential is given by eqn (12.5.5):

\[
W_1 = \frac{4\pi e^{-s}}{2} \delta \exp\left[-(r-\delta)/\lambda_d\right]
\]

with \( \delta \) given by eqn. (7.11.6): \( \delta \equiv \varphi_0/[4\pi e\sigma(1+\kappa \sigma)] = 2 z e/[4\pi e\delta(1+\delta/2\lambda_d)] \)

(This assumes that the interaction is too small to affect the charge on the particles.)

14.2.4 \( 4\pi \sigma^2/3 = 1/\rho \) (14.2.9) ; \( \phi = \pi \sigma^3/6 \) (14.1.2)

\( a = (3/4\pi \rho)^{1/3} - (3\delta^3/4\pi \cdot 6\phi)^{1/3} = \delta/2\phi^{1/3} \)

14.2.5(a) \( \gamma = [z^2 e^2 \exp(\kappa \delta)]/[4\pi e \delta kT(1 + \kappa \delta/2)] \) (14.2.11b)

Using eqn. (7.11.6) in the form \( \varphi_0 = 2ze/[4\pi e \delta(1+\kappa \delta/2)] \) we have:

\[
\gamma = \frac{\varphi_0^2 [4\pi e \delta(1 + \kappa \delta/2)^2 \exp(\kappa \delta)]}{4\pi e \delta kT(1 + \kappa \delta/2)^2} = \frac{\pi e \delta \varphi_0^2}{kT} \exp(\kappa \delta)
\]

(b) Using (7.11.6) in the form: \( z e/[\pi \delta^2] = \sigma = 2e\psi_d(1 + \kappa \delta/2)/\delta \) and substituting in the previous expression:

\[
\gamma = \frac{\sigma \delta^3 \exp(\kappa \delta)}{[\epsilon(2 + \kappa \delta)^2 kT]}
\]

14.4

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Exercises. 14.3.1 Given the neutron rest mass $m_n = 1.67494 \times 10^{-27}$ kg, calculate the velocity of a neutron whose thermal energy corresponds to a temperature (a) $T = 293$ K, (b) $T = 20$ K. Are relativistic effects important? Calculate the de Broglie wavelengths corresponding to these velocities, and compare the neutron energies with those of X-ray photons at the same wavelengths.

14.3.2 Calculate the electron densities ($e/m^3$) in (a) $C_6H_{15}OH$, (b) $C_3H_{18}$, (c) $C_2H_5OH$, (d) $Al_2O_3$, (e) $SiO_2$, (f) $H_2O$, and (g) $D_2O$. Take the respective densities as 825, 704, 790, 3970, 2655, 1000, and 1100 kg/m$^3$.

14.3.3 Use Table 14.1 to calculate the neutron scattering amplitude densities (m/m$^2$) corresponding to the electron densities found in the previous exercise. Compare the relative light scattering contrasts (scattering density differences) between the various materials with those for neutron scattering. How does the mean potential (14.3.2) compare with $kT$ for each material at room temperature?

14.3.4 Use the results of Exercises 14.3.3 to evaluate eqn (14.3.9) at $Q = 0$ for a uniform silica particle in $H_2O$. Show how a measurement of this intensity can be used to find the mass of the particle. Does the result depend on particle shape? [Note that this procedure can be used to evaluate the molar mass of any particle, e.g. a protein in dilute solution.]

14.3.5 What mixture of $H_2O$ and $D_2O$ would make the $Al_2O_3$ invisible to neutrons in a mixed $Al_2O_3/SiO_2$ dispersion, so that $SiO_2 - SiO_2$ correlations could be studied directly? (Assume ideal mixing and ignore hydration effects.) Is there an equivalent solvent mixture for light scattering?

14.3.6 The refractive index, normally thought of as a ‘wave’ property, was derived in eqn (14.3.3) using a purely particle kinetic energy. See, for example, Bacon (1975) for a derivation based entirely on wave mechanics. (This is a rather striking example of wave - particle duality.) Many examples of ‘neutron optical’ experiments, such as interferometry, are given by Klein and Werner (1983).

14.3.7 Satisfy yourself the eqns. (14.3.5) and (14.3.6) are equivalent.

14.3.8 (a) Show that, when $B(r)$ depends only on $r = |r|$, eqn (14.3.8) reduces to the Debye result

$$F(Q) = 4\pi \int [B(r) - B_m] r^2 \sin(Qr)/(Qr) \, dr$$

[Hint. Choose spherical polar coordinates centred on the particle and evaluate the angular integrals using the hints suggested in exercise (13.6.3).]

(b) Use part (a) to derive the form factor for a sphere of radius $a$ and uniform scattering amplitude density $B_0$:

$$F(Q) = 3V(B_0 - B_m)[\sin(Qa) - Qa \cos(Qa)]/(Qa)^3$$

where $V$ is the volume of the sphere.

/ 4. 5
14.3.9 Justify the Guinier plot of \( \ln I(Q) \) against \( Q^2 \) for determining the radius of gyration of a polymer molecule using the series expansions for \( \sin \) and \( \cos \) in equation (14.3.11).

**Solutions**

14.3.1 \[ m_n = 1.67494 \times 10^{-27} \text{ kg} \]

For \( T = 293 \text{ K}, \ 3kT/2 = 6.065 \times 10^{-21} \text{ J} \)

\[ \text{Kinetic energy} = \frac{1}{2} m v^2 \ 	ext{so} \ v = (7.242 \times 10^6 \text{ m/s}) = 2.691 \times 10^3 \text{ m/s}. \]

(b) At \( T = 20 \text{ K}, \ 3kT/2 = 4.14 \times 10^{-22} \text{ J} \); \[ \overline{v} = 7.031 \times 10^3 \text{ m/s}. \]

Relativistic effects are insignificant in both cases.

The de Broglie wavelength at 293 K is:

\[ \lambda = h/\bar{p} = h/m\overline{v} = 6.627 \times 10^{-34} /[1.6749 \times 10^{-27} \times 2691] = 0.147 \text{ nm} \]

At 20 K it is 5.627 nm. Neutron particle energy at 293 K is \( \frac{1}{2} m v^2 = 6.065 \times 10^{-21} \text{ J} \).

Photon energy at 0.147 nm is \( h\nu - h c/\lambda = 6.627 \times 10^{-34} \times 3 \times 10^8 \times 0.147 \times 10^{-9} = 1.35 \times 10^{-15} \text{ J} \)

(~2 \times 10^5 larger).

The photon energy at 5.627 nm is \( 3.5 \times 10^{-17} \text{ J} \) which is about \( 10^5 \) larger than the neutron energy.

14.3.2 Calculation for \( \text{C}_4\text{H}_9\text{OH} \). Density = 825 kg m\(^{-3}\); MW = 250; No of electrons per molecule = 134.

Electron density = \( 134 \times 6.023 \times 10^{26} \times 825/250 = 2.663 \times 10^{29} \text{ m}^{-3} \).

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \text{C}_4\text{H}_9\text{OH} )</th>
<th>( \text{C}_2\text{H}_5\text{OH} )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{D}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (kg m(^{-3}))</td>
<td>704</td>
<td>790</td>
<td>3970</td>
<td>2655</td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>MW</td>
<td>114</td>
<td>46</td>
<td>129</td>
<td>63</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>( e^- / \text{molecule} )</td>
<td>66</td>
<td>26</td>
<td>50</td>
<td>30</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>Electron density ( \times 10^{-29} )</td>
<td>2.455</td>
<td>2.689</td>
<td>4.782</td>
<td>7.615</td>
<td>3.346</td>
<td>3.313</td>
</tr>
</tbody>
</table>

Note that all fall within a factor of about 3.
14.3.3

<table>
<thead>
<tr>
<th>Substance</th>
<th>C₇H₅OH</th>
<th>C₆H₅</th>
<th>C₈H₁₆</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>H₂O</th>
<th>D₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho )</td>
<td>825</td>
<td>704</td>
<td>790</td>
<td>3970</td>
<td>2655</td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>MW</td>
<td>250</td>
<td>114</td>
<td>46</td>
<td>129</td>
<td>63</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>( R(\times 10^{14}) ) m⁻²</td>
<td>-0.166</td>
<td>-0.526</td>
<td>-0.346</td>
<td>4.507</td>
<td>4.000</td>
<td>-0.561</td>
<td>6.345</td>
</tr>
</tbody>
</table>

Note that \( B \) varies from negative to positive values and in absolute value over about a factor of 35-40 times, whereas the electron density (which determines light scattering behaviour) is always positive and varies only over a factor of about three.

To calculate \( U/kT \) we need to multiply the \( B \) value by \( \hbar^2/(2\pi m_kT) \) = 0.0101\times10⁻⁶⁺²⁷⁻²³ = 1.01\times10⁻²⁰ m², so the mean potential is only 10⁻⁶ of the thermal energy.

14.3.4 Note that \( \lim ( \text{as } Q \to 0 ) [\sin Qr] / Qr = 1 \) then

\[
\lim_{Q \to 0} F(Q) = 4\pi \int [B\langle r \rangle - B_m] r^2 dr
\]

and \( B\langle r \rangle \) is independent of \( r \) for a uniform particle. Hence:

\[
F(0) = \frac{4\pi}{3} \rho^3 [B(\text{silica}) - B(H₂O) \text{ (in m)}]
\]

\[
F(0) = \frac{1}{\rho} \int [B(\text{silica}) - B(H₂O)] dV = [B(\text{silica}) - B(H₂O)] m / \rho
\]

where \( m \) is the particle mass and \( \rho \) is its density.

\( B(\text{silica}) - B(H₂O) = |4.000 + 0.561|\times10^{14} \text{ m}² \) and \( \rho = 2655 \text{ kg m}^{-3}. \)

Therefore \( m = [2655\times10^{14}/4.561] \times 9 \times 10^{-3} \text{ m}³/\text{m}² \). Mass (in g) = 5.821\times10⁻³ [F(0) in m].

This result is independent of shape but is only so for a uniform particle.

14.3.5 Given \( B \) for Al₂O₃ is 4.507 and for D₂O it is 6.345 and for water -0.561, suppose \( x \) is the mole fraction of water to D₂O then we require:

\[
4.507 = x \times -0.561 + (1-x)6.345 \text{ so that } B_m = B(\text{Al}_2\text{O}_3) \text{ i.e. } x = 0.266
\]

So we use a mixture of 0.266 moles of water and 0.734 moles of D₂O. This would mean 0.266\times18 = 4.788 g of water and 14.68 g of D₂O so the % by mass of water is 24.6%.

It may be possible to find a mixture of water and some (water soluble) organic solvent which matches the refractive index of alumina in the visible region, say, and not that of SiO₂ but that is unlikely. Certainly it cannot be done with water and D₂O.
14.3.6 Requires no solution.

14.3.7 Refer to Exercise 13.7.1 and the discussion surrounding equation 13.7.3. The calculation of the modulus in eqn (14.3.5) corresponds to multiplying \( \exp(iQ \cdot R_j) \), \( \exp(-iQ \cdot R_k) \) and gives \( e^0 = 1 \) for all \( j \). The cross terms which come from cross multiplying terms in the series give rise to the \( iQ \cdot (R_j - R_k) \) terms and are retained in the second equation (14.3.6) but the terms involving \( (R_j - R_k) \) again give \( e^0 = 1 \) but they are not included in this formulation because they correspond to the single atom (incoherent) effects.

14.3.8(a)

\[
F(Q) = \sum_j h_j \exp(iQ \cdot r_j) = \int [B(r) - B_m] \exp(iQ \cdot r) dr \tag{eqn.14.3.9}
\]

\[
> = \int d\phi \int_0^\pi \sin \theta \cdot d\theta \cdot r^2 [B(r) - B_m] \exp(iQ \cdot r) dr
\]

\[
= 2\pi \int_0^\pi \sin \theta d\theta [B(r) - B_m] r^2 \exp(iQ \cos \theta) dr
\]

\[
= 2\pi \int_0^\infty [B(r) - B_m] r^2 \left\{ \int_0^{\pi} \exp(iQ \cos \theta) \cos \theta d\theta \right\} dr
\]

\[
= 2\pi \left\{ \int_0^\infty [B(r) - B_m] r^2 \frac{1}{iQR} \left\{ \exp(iQ \cos \theta) \right\}_0^{\pi} dr \right\}
\]

\[
= 2\pi \int_0^\infty [B(r) - B_m] r^2 \left\{ \frac{1}{iQR} \left\{ \exp(-iQr) - \exp(iQr) \right\} \right\} dr
\]

\[
= 4\pi \int [B(r) - B_m] r^2 \{ \sin(Qr) \} dr
\]

(b) \( F(Q) = 4\pi \int [B(r) - B_m] r^2 \sin Qr \, dr/Qr \) and for a sphere of radius \( a \) of uniform density, \( B_0 \):

\[
F(Q) = 4\pi \int [B_0 - B_m] r^2 \sin Qr \, dr/Qr
\]

---

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\[ \begin{align*} 
&= 4\pi \int_{0}^{a} \left( B_0 - B_m \right) \frac{r}{Q} \sin Qr \, d(Qr) = 4\pi \int \left( B_0 - B_m \right) \left( \frac{r}{Q^2} \, d\cos Qr \right) \, dr \\
&= 4\pi \left( B_0 - B_m \right) \frac{1}{Q^2} \left[ -r \cos Qr + \int \cos Qr \, dr \right]_{0}^{a} = \frac{4\pi \left( B_0 - B_m \right)}{Q^2} \left[ \frac{\sin Qa}{Q} - a \cos Qa \right] \\
&= \frac{3V(B_0 - B_m)}{(Qa)^3} \left[ \sin Qa - Qa \cos Qa \right]
\end{align*} \]

14.3.9

\[ F(Q) = \frac{3V(B_0 - B_m)}{(Qa)^3} \left[ \sin Qa - Qa \cos Qa \right] \quad \text{and} \quad \hat{R}(Q) = N_p V_p^2 (B_0 - B_m)^2 F^2(Q) \]

Recall from Exercise 3.3.4 that for small $Qa$: \[ P(\theta) = F^2(Q) = 1 - (Qa)^2/5 + \ldots \]
so \[ \hat{R}(Q) = N_p V_p^2 (B_0 - B_m)^2 [1 - (Qa)^2/5 + \ldots] \]

Then \[ \ln \hat{R}(Q) = A + \ln [1 - (Qa)^2/5] = A - (Qa)^2/5 \quad \text{for small values of } Qa. \]

The plot of $\ln \hat{R}(Q)$ against $Q^2$ (or $\sin^2 \theta$) is the Guinier plot (where $\theta$ is the scattering angle (eqn. 3.3.17)).

**Exercise 14.5.1 Establish eqn (14.5.5).**

---

**Solution**

\[ R = \frac{16\pi^2}{Q^4} \left[ (B_0 - B_m)^2 + (B_2 - B_1)^2 + 2(B_0 - B_1)(B_2 - B_m) \cos Qd \right] \]

For $B_1 = B_2 = B$: \[ R = \frac{16\pi^2}{Q^4} \left[ (B_0 - B)^2 + (B - B_2)^2 - 2(B_0 - B)^2 \cos Qd \right] \]

\[ = \frac{32\pi^2}{Q^4} (B_0 - B)^2 [1 - \cos Qd] = \left[ \frac{8\pi(B_0 - B)}{Q^2} \frac{\sin Qd}{2} \right]^2 \]

\[ 14 \cdot q \]
Chapter 15
Solutions

Exercises. 15.2.1 The following shear stress/shear rate data were obtained on a meat extract at 77° C (Boger et al. 1980). (The first element of each number pair is shear rate ($\dot{\gamma}$) and the second is shear stress (N m$^{-2}$):

0.111, 18.04; 0.140, 18.32; 0.176, 18.65; 0.222, 19.09; 0.279, 19.62;
0.352, 20.31; 0.443, 21.16; 0.557, 22.24; 0.702, 23.60; 0.883, 25.30;
1.112, 27.45; 1.400, 30.16; 1.762, 33.56; 2.218, 37.85; 2.793, 43.25;
3.516, 50.05; 4.426, 58.60; 5.576, 69.41; 7.015, 82.94; 8.831, 100.01;
11.117, 121.50; 14.00, 148.60.

Plot $S$ versus $\dot{\gamma}$ on linear paper and on log -- log paper and hence determine the characteristics of this fluid in terms of eqns (15.2.6) and (15.2.7).

15.2.2 Show that the Meter model of Table 15.1 corresponds to eqn (15.2.9) with $\alpha = 2$.
What are the relations between the de Haven and Ellis parameters? Why does the Ellis model break down at very high shear rates?

15.2.3 The following shear stress/shear rate data were obtained on an aqueous solution of methyl cellulose at 18° C. (Boger et al. 1980). (The first figure is shear rate ($\dot{\gamma}$) and the second is shear stress (N m$^{-2}$)).

0.140, 0.117; 0.1762, 0.141; 0.2218, 0.169; 0.2793, 0.211; 0.3516, 0.281;
0.4426, 0.352; 0.5572, 0.446; 0.7015, 0.563; 0.8831, 0.687; 1.1117, 0.847;
1.400, 1.076; 1.762, 1.305; 2.218, 1.625; 2.793, 2.010; 3.516, 2.53;
4.426, 3.08; 5.572, 3.79; 7.015, 4.68; 8.831, 5.41; 11.117, 6.53; 14.000, 8.11;
17.620, 9.46; 22.18, 11.49; 27.93, 13.52; 35.16, 16.22; 44.26, 18.92;
55.72, 22.10; 70.15, 26.13; 88.31, 30.00; 111.17, 34.80; 140.00, 40.0;
176.2, 45.7; 221.8, 52.5; 279.3, 57.6.

See how well they fit a power law (log - log) plot over limited ranges of shear rate. State the shear ranges over which a reasonable straight line fit is obtained and estimate the parameters $K$ and $n$ applicable to those regions.

15.2.4 Recast the Ellis model in the form $\dot{\gamma} = a(S + bS^n)$ and show that it gives a good fit to the data of Exercise 15.2.3 over the whole range of $\dot{\gamma}$ using the parameters $\eta_0 = 0.794$ N
m^2 s, S_i = 21.554 N m^2 and α = 2.027.

Compare this with the fit using eqn (15.2.9) with a suitable choice of η_w. (That is the
Meter model with α = 2.)

**Solutions**

15.2.1 The figure shows the plot of the
data which shows a small yield value and
a linear response above that value. It
would be represented by an expression of
the form:

\[ S = S_0 + \eta \dot{\gamma} \]

This is Herschel-Bulkley behaviour with
\( n = 1 \) and \( K = \eta \), which is a rather trivial
departure from Newtonian behaviour.
There is no point in plotting the data on a
log-log scale.

15.2.2(a) The Meter model from Table 15.1 is:

\[ \frac{S}{\dot{\gamma}} = \eta = \eta_w + \frac{(\eta_0 - \eta_w)}{1 + (S/S_i)^{\alpha-1}} \]

For \( \alpha = 2 \) this gives

\[ \frac{\eta - \eta_w}{\eta_0 - \eta_w} = \left(1 + \frac{S}{S_i}\right)^{-\alpha} = \left[1 + \frac{S}{S_i}\right]^{-1} \]

(b) de Haven:

\[ S/\dot{\gamma} = \eta = \eta_0[1 + CS_i] \]

Ellis:

\[ S/\dot{\gamma} = \eta = \eta_0[1 + (S/S_i)^{\alpha-1}] \]

The relation is \( C = S_i^{1-\alpha} \) and \( S^\sigma = S^\sigma \) or \( \alpha = 1 + n \) so \( C = S_i^{-\alpha} \)

The Ellis model breaks down at very high shear rates because it does not recognise the existence
of a high shear limiting value to the viscosity. (Shear dependent structure can be reduce to zero.)

S15.2
15.2.3

The Figure on the left shows all of the shear data plotted on a log-log plot. The regression line is not a bad fit but it is clear that the data follow a curve. The data can be broken into low, medium and high shear regions and these show better fits to log-log relation (Herschel-Bulkley or Ostwald-de Waele). The figure on the right shows the low shear rate data. The lower figures are for intermediate and high shear rates.

\[ \log(\text{shear stress}) = \log(\text{shear rate}) \times n + \log(k) \]

\[ \log(n) \text{ and } \log(k) \text{ parameters can be obtained by linear regression analysis for these plots and the values obtained are shown in the Table below.} \]

\[ \text{S15.3} \]

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15.2.4 To check the Ellis model we need values of \( \eta \) as a function of shear rate \( S \) and these are obtained from \( \eta = \frac{S}{\dot{\gamma}} \) from which we obtain \( \eta_0 \). (See figure.)

The data is rather scattered at the low shear end but a value of 0.8 Pa s would appear to be appropriate. It is apparent that the data have not been taken to high enough shear rates to reach \( \eta_\infty \). That parameter would have to be less than 0.25 Pa s and would not affect the data in the figure. As can be seen from Fig 15.2.3 in the text, the Ellis and Meter models are identical until the viscosity begins to level off at the high shear rate end.

\[
\frac{S}{\dot{\gamma}} = \eta = \frac{\eta_0}{1 + (SS)^{\alpha-1}} \quad \text{so} \quad \dot{\gamma} = \frac{1}{\eta_0} \left( S + \frac{S^{\alpha}}{S_0^{\alpha-1}} \right) \quad \text{and} \quad \alpha = 1/\eta_0 \quad , \quad b = S_0^{1-\alpha} \quad , \quad \alpha = m
\]
Solutions to Exercises

Chapter 15 Part 2.

Exercises. 15.5.1 Establish eqns (15.5.4) and (15.5.6).

15.5.2 Assuming that for an ideal Bingham fluid one can write shear rate \( \dot{\gamma} = -r \, d\omega/dr = (S - S_B)/\eta_{PL} \), derive the Reiner - Riwlin eqn (15.5.8) assuming that the fluid is moving with angular velocity \( \Omega \) at the inner cylinder \( r = R_b \) and zero only at the outer cylinder \( r = R_c \).

15.5.3 Show that if the Bingham yield value, \( S_B \), is such that only some of the fluid is moving \( S_C < S_B < S_\ast \) (where \( S_C \) and \( S_\ast \) refer to outer (cup) and inner (bob) cylinders) then the critical radius beyond which the fluid is stationary is \( R_{\text{crit}} = R_b(S_B/S_b)^{\frac{1}{n}} \). Hence show that the critical stress \( S_{\text{crit}} \) (measured at the bob) which must be exceeded so that flow occurs throughout the annulus is given by \( S_{\text{crit}} = S_b(R_c/R_b)^{\frac{1}{n}} \).

15.5.4 Show that the Reiner-Riwlin equation (15.5.8) can be written in the form

\[
\dot{\gamma} = \frac{(S_b - S_B)\Omega}{T_0 k_1 - S_b k_2} = \dot{\gamma}
\]

where \( k_1 \) and \( k_2 \) are apparatus constants. (The data in the linear regime (where \( T_0 = \Omega \) is treated by plotting this function \( \dot{\gamma} \) against \( S_b \) = \( T_0/2\pi R_b^2 L \) and determining the slope (which is \( \eta_{PL} \)).)

15.5.5 For the power law fluid \( S = K_b(-r d\omega/dr)^n \) in a coaxial cylinder viscometer we have

\[
T_0 - S.2\pi r^2 L = K_b(-r d\omega/dr)^n. 2\pi r^2 L.
\]

Integrate this expression between the limits \( \omega = 0 \) and \( \Omega \) and \( r = R_c \) and \( R_b \) (i.e. stationary outer cylinder) to obtain:

\[
\Omega = (n/2)\{T_0/2\pi K_b L\}^{1/n}(1/R_b^{2n} - 1/R_c^{2n})
\]

S15.5

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Hence show that

$$\ln \Omega = (1/n) \ln S_b + \ln \left( \frac{n K_1^{-1/n}}{2} \left[ 1 - (R_b/R_c)^{2/n} \right] \right).$$

(A plot of $\ln \Omega$ against $\ln S_b$ (or $\ln T_0$) gives a slope from which $n$ is obtained and so $K_1$ can be evaluated from the general expression for $S$ (Table 15.1).)

15.5.6 According to eqn (4.8.1), the Reynolds number is given by $Re = \rho V_b \eta$ which for the Couette viscometer with a rotating bob becomes $(Re)_{crit} = [V_b (R_c - R_b) \rho/\eta]_{crit}$ where $V_b$ is the (linear) velocity of the bob ($= v_b$). Estimate the velocity gradient at which one would anticipate that water would exhibit instability in a Couette viscometer with $R_b = 3$ cm, $R_c = 3.1$ cm. (Take $\eta = 10^{-3}$ N m$^{-1}$s and $\rho = 10^3$ kg m$^{-3}$.) (Hint: refer to Exercise 4.7.4.)

---

**Solutions**

15.5.1 Torque $T = 2\pi r^2 LS$ is constant so $4\pi r S \, dr + 2\pi r^2 L \, dS = 0$ or $dr/r = -dS/2S$ (eqn(15.5.4))

From (15.5.2) $\frac{d\omega}{\omega} = -f(S) dr/r = V_2 \int f(S) \frac{dS}{S}$

$$\therefore \int \frac{d\omega}{\omega} = -\Omega = V_2 \int f(S) \frac{dS}{S}$$

15.5.2 In this case also the torque on every cylinder of fluid in the gap is the same as the torque on the inner cylinder. The shear stress on each cylinder is:

$$S = \eta \left( \frac{d v}{d r} - \frac{v}{r} \right) + S_b$$

Then $T_0 = 2\pi r [\eta \left( \frac{d v}{d r} - \frac{v}{r} \right) + S_b] l$

S15.6
which should be compared with eqn (4.7.3). Rearranging:

\[ \frac{dv}{dr} - \frac{v}{r} = r \frac{d(v)}{dr} = \frac{T_0}{2\pi \eta' r^2} - \frac{S_B}{\eta'} \]

(See Exer. 4.7.1)

So

\[ \frac{d(v)}{r} = \left[ \frac{T_0}{2\pi \eta' r^3} - \frac{S_B}{\eta'} \right] dr \]

\[ \int \frac{d(v)}{r} = \frac{-T_0}{4\pi \eta' r^2} + \frac{S_B \ln r}{\eta'} + C_1 \]

where \( C_1 \) is obtained from the fact that \( v = 0 \) at the inner surface where \( r = R_b \):

\[ C_1 = \frac{T_0}{4\pi \eta' R_b^2} + \frac{S_B \ln R_b}{\eta'} \]

Also \( v = \Omega R_0 \) at the outer cylinder so:

\[ \frac{\Omega R_c}{R_c} = \Omega = \left[ \frac{T_0}{4\pi \eta' R_b^{2}} \left( \frac{1}{R_b^{2}} - \frac{R_c^{2}}{R_c^{2}} \right) - \frac{S_B \ln R_c}{\eta' R_c^{2}} \right] \]

15.5.3 The torque is the same on each cylinder of fluid, but the stress increases from the outside to the inside (\( S \) is proportional to \( \Omega r^2 \)). The critical stress is \( S_B \), so if \( S > S_B \) the material will flow.
\[
\frac{R_{\text{crit}}}{R_b} = \left[ \frac{S_b}{S_0} \right]^\frac{95}{S_b} = \left[ \frac{S_b}{S_b} \right]^\frac{95}{S_b} \text{ since } T \text{ is constant.}
\]

So
\[
R_{\text{crit}} = R_b \left[ \frac{S_b}{S_b} \right]^\frac{95}{S_b}.
\]

If this critical stress is to be established at the outside cylinder (so that all of the material is subjected to at least the stress \(S_b\)) then we require \(R_{\text{crit}} = R_b\) and so
\[
S_{\text{crit}} = \frac{R_b^2}{R_b} S_b
\]

15.5.4 Shear rate = \(\dot{\gamma}\) for the Reiner-Riwlin fluid = \((S_b - S_0)\eta_{PL}\)

\[
\dot{\gamma} = \frac{1}{\eta_{PL}} \left[ \frac{T_0}{2 \pi r^2 L} - S_b \right]
\]

\[
= \frac{1}{\eta_{PL}} [S_b - S_b]
\]

\[
\dot{\gamma} = \eta_{PL} \left[ \frac{T_0}{2 \pi r^2 L} - S_b \right] - S_b
\]

But from exercise (15.5.51)

\[
\eta_{PL} = \left[ \frac{T_0}{4 \pi L \Omega} \left( \frac{1}{R_b^2} - \frac{1}{R_c^2} \right) - \frac{S_b\ln R_s}{\Omega R_b} \right]
\]

\[
= \frac{k_1}{T_0} - \frac{k_2 S_b}{\Omega}
\]

where \(k_1\) and \(k_2\) depend only on the apparatus characteristics.

\[
\therefore \dot{\gamma} = \frac{(S_b - S_b)}{k_1 T_0 - k_2 S_b} \Omega.
\]
15.5.5 \( T_0 = S \cdot 2\pi^2 L = K_1(-r\omega/dr)^n \cdot 2\pi^2 L \) for a power law fluid. So:

\[
\frac{d\omega}{dr} = \left[ \frac{T_0}{K_1 \cdot 2\pi L} \right]^{1/n} \cdot \frac{1}{p^{1+2/n}} \cdot 1/(1 - 1)^n
\]

\[
\int_0^\varpi d\omega = \frac{T_0}{2\pi K_1 L} \cdot (-1)^{2-n} \cdot \int_{R_c}^{R_b} \frac{dr}{r^{1+2/n}}
\]

\[
\varpi = \left[ \frac{T_0}{2\pi K_1 L} \right]^{1/n} \cdot \frac{1}{2} \left( \frac{1}{R_b^{2/n}} - \frac{1}{R_c^{2/n}} \right)
\]

So \( \ln \varpi = \frac{1}{n} \ln \left[ \frac{T_0}{2\pi L} \right] + \ln \left[ \frac{1}{2} K_1^{-1/n} \left( \frac{1}{R_b^{2/n}} - \frac{1}{R_c^{2/n}} \right) \right] \)

But \( T_0/2\pi L = S_b R_b^2 \) from the initial equation so

\[
\ln \varpi = \frac{1}{n} \ln S_b + \ln \left[ \frac{1}{2} K_1^{-1/n} \left( 1 - \left( \frac{R_b}{R_c} \right)^{2/n} \right) \right]
\]

15.5.6 \( \nu_\text{c} = V^2/R_c = R_d \rho \frac{\varpi \rho}{\eta} = V^2(R_c - R_b) \rho \frac{\varpi \rho}{\eta} = 10^3 \nu_\text{c} \). If the velocity gradient in the gap is \( V' \) then \( V' = \varpi R_d / (R_c - R_b) - 30 \) and \( \nu_\text{c} = R_d \varpi = V (R_c - R_b) \) so \( \nu_\text{c} = V (\text{sec}^{-1}) \)

Turbulent instabilities occur in cylindrical tubes at Reynolds numbers of order 2000 and one might expect similar values to be required for the critical velocity gradient in a Couette. In fact they occur at much lower values if the inner bob is rotating.
Exercises. 15.6.1 Derive eqn (15.6.2a) assuming that $dp/dz$ is constant for fully developed flow. Rewrite eqn (15.6.1a) in terms of the deviatoric stresses $p_{rr}$ and $p_{00}$ and hence show that (Boger et al. 1980):

$$p_{rr} = p + p(0,z) - \frac{1}{r} \int_0^r (p_{rr} - p_{00}) d\ln r = 0.$$

Hence derive eqns (15.6.2b) and (15.6.2c).

15.6.2 Derive eqn (15.6.10) using eqns (15.6.5) and (15.6.9).

15.6.3 Derive eqn (15.6.12). What is the effect on the pressure gradient of increasing the velocity fourfold when the flow behaviour index $(n)$ is 0.3? Compare this with a fourfold increase in velocity for a Newtonian fluid.

15.6.4 Derive eqn (15.6.16) and then show that, for a power law fluid with index $n, b = \frac{1}{n}$.

15.6.5 Show that eqn (15.6.12) can be written in the form (Boger et al. 1980):

$$\ln \dot{Q} = \ln \left[ \frac{1}{2K} \right]^{\frac{1}{3n}} \pi \left( \frac{n}{3n + 1} \right) \left[ \frac{n+1}{3n+1} \right] + \frac{1}{n} \ln \frac{\Delta \rho}{\rho_0}.$$

The plot of $\ln \dot{Q}$ versus $\ln (\Delta \rho/\rho_0)$ (which corresponds to $\ln (8\dot{\theta}/D)$ versus $\ln (a\Delta \rho/2L)$) should give a straight line of slope $1/n$. The intercept then gives a value of $K$. Show that the apparent viscosity, $\eta$, is $\eta = K^{1/n} \eta_0^{(1-1/n)}$ which can, hence, be evaluated for any wall stress $\tau_w = a\Delta \rho/2L$.

15.6.6 The power law parameters for a low density polythene at 190 °C are $n = 0.72$ and $K = 13400$ N s$^n$ m$^2$ and are valid for $0.0214 \leq \dot{\theta} \leq 0.427$. Calculate the minimum and maximum volume and mass flow rates which this material experiences at these extreme shear rates when flowing through a long cylindrical die of diameter 4 cm. (The density of the polyethylene at 190 °C is 900 kg m$^{-3}$.) (Mass flow $= W = \rho V A$ where $A$ is the cross-sectional area of the die.) (Hint: check Exercise 15.6.4.)

S15.10

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15.6.7 Note that from eqn (15.6.16) the quantity $4Q/\pi a^3 = 8VD$ is equal to the wall shear rate only if $b = 1$ (Newtonian fluid). Show that the approximate apparent viscosity $\eta_a = S_w/(8VD)$ based on this approximate estimate of the wall shear rate is related to the true apparent viscosity, $\eta$, for an inelastic fluid by the expression:

$$\frac{1}{\eta} = \frac{1}{\eta_a}\left[1 - \frac{1}{4}\frac{d\ln\eta_a}{d\ln S_w}\right]$$

This equation (due to Philippoff 1942) can be used to correct data ($\eta_a$) based on uncorrected shear rates to those ($\eta$) based on true values (van Wazer 1963, p. 193).

**Solutions**

15.6.1. Since $dp/dr$ is constant for fully developed flow we have, from 15.6.1 (c)

$$\frac{dr}{dr} = (1/r)\frac{d(r\sigma_{ez})}{dr} = C \quad \text{so} \quad d(r\sigma_{ez}) = Cr dr$$

$$r\sigma_{ez} = Cr^2/2 \quad \text{so} \quad \sigma_{ez} = \frac{Cr^2}{2}$$

15.6.2 $\sigma_{ez} = S_w/r/a$ and $-d\varepsilon_z/dr = f(\sigma_{ez})$

$$Q = \int_0^a r^2 dv_z = \pi \int_0^a r^2 f(\sigma_{ez}) dr$$

$$d\sigma_{ez} = \frac{S_w}{a} dr \quad \text{so} \quad Q = \pi \frac{S_w}{a} \int_0^a r^2 f(\sigma_{ez}) d\sigma_{ez}$$

$$Q = \frac{\pi a}{S_w} \int_0^{S_w} \frac{\sigma_{ez}^2}{S_w^2} f(\sigma_{ez}) d\sigma_{ez} \quad \text{so} \quad \frac{Q}{\pi a^3} = \frac{1}{S_w} \int_0^{S_w} \frac{\sigma_{ez}^2}{S_w^2} f(\sigma_{ez}) d\sigma_{ez}$$

15.6.3

S15.11

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\[
\frac{Q}{\pi a^3} = \frac{1}{S_w} \int_0^{S_v} \sigma_{rz}^2 f(\sigma_{rz}) d\sigma_{rz}. \quad \text{If} \quad \sigma_{rz} = K \left( -\frac{dv_z}{dr} \right)^n \quad \text{so that}
\]

\[
f(\sigma_{rz}) = -\left( \frac{dv_z}{dr} \right) = \left( \frac{\sigma_{rz}}{K} \right)^{1/n}
\]

Then \[
\frac{Q}{\pi a^3} = \frac{1}{S_w} \int_0^{S_v} \sigma_{rz} \frac{\sigma_{rz}^{1/n}}{K^{1/n}} d\sigma_{rz} = \left( \frac{1}{K} \right)^{1/n} \frac{1}{S_w} \int_0^{S_v} \sigma_{rz}^{(2+1/n)} d\sigma_{rz}
\]

\[
\frac{Q}{\pi a^3} = \frac{n}{3n+1} \frac{1}{S_w} \left[ \int_0^{\sigma_{rz}} \left( \frac{\sigma_{rz}}{K} \right)^{1/n} \right]^{S_v} = \frac{n}{3n+1} \left[ \frac{a}{2K} \frac{dp}{dz} \right]^{1/n}
\]

from (15.6.4).

Average fluid velocity \[\frac{Q}{\pi a^2} = \frac{na}{3n+1} \left( \frac{1}{2K} \frac{dp}{dz} \right)^{1/n}.\]

If this increases by a factor of 4 then \((dp/dz)^{10/3}\) increases by a factor of 4 so \(dp/dz\) increases by a factor of \(4^{0.3} = 1.52\). For a Newtonian fluid, from Table 15.2 if \(Q/\pi a^2\) increases 4 fold then so too does \(S_w\) and so does \((dp/dz)\) from eqn (15.6.4).

15.6.4

\[
\frac{Q}{\pi a^3} = \frac{1}{S_w} \int_0^{S_v} \sigma_{rz}^2 f(\sigma_{rz}) d\sigma_{rz} \quad \text{So} \quad \frac{S_w Q}{\pi a^3} = \int_0^{S_v} \sigma_{rz}^2 f(\sigma_{rz}) d\sigma_{rz}
\]

S15.12
Differentiation w.r.t. \( S_w \) gives:

\[
\frac{1}{\pi a^3} \left[ 3QS_w^2 + S_w^3 \frac{dQ}{dS_w} \right] = S_w^2 f(S_w) = S_w^2 \left( -\frac{dv_z}{dr} \right)_{r=a} = S_w^2 \frac{d\gamma}{dr}
\]

\[
dS_w/S_w = d\ln S_w = d\ln \Delta p = d\Delta p / (\Delta p).
\]

Therefore:

\[
\gamma = \frac{1}{\pi a^3} \left[ 3Q + \frac{dQ}{d\ln S_w} \right] = \frac{1}{\pi a^3} \left[ 3Q + \frac{dQ}{d\ln \Delta p} \right] (15.6.14)
\]

\[
= \frac{Q}{\pi a^3} (3 + b) = \frac{1}{4} (3 + b) \frac{8V'}{D} (15.6.16)
\]

(Note that \( d\ln (A/Q) / d\ln (B\Delta p) = d\ln Q / d\ln \Delta p \) if \( A \) and \( B \) are constants.

The more messy form of \( b \) (eqn (15.6.15) relates to the parameters which are used in the formulations in Table 15.2.

The term \( 4Q/\pi a^3 \) is the shear rate at the wall and \((\alpha \Delta p/2L)\) is the shear stress at the wall so for the general power law fluid: \( \sigma = K \gamma^n \quad \ln \sigma = \ln K + n\ln \gamma \) and \( d\ln \gamma / d\ln \sigma = 1/n - b \).

15.6.5

\[
\frac{Q}{\pi a^3} = \frac{n}{3n - 1} \left[ \frac{a}{2K} \frac{d\rho}{dz} \right]^{1/n} (15.6.12)
\]

\[
\ln Q = \ln \left[ \frac{n}{3n - 1} \left( \frac{1}{2K} a^{(3 - i/n)} \right) \right] + \frac{1}{n} \ln \frac{\Delta p}{L}
\]

S15.13
where \( \Delta p/L = \frac{d\rho}{dz} \). The intercept is the logarithm term and since \( n \) is available from the slope and \( a \) is known, this allows \( K \) to be evaluated. But \( S = K \dot{\gamma}^n \) and \( \eta_{\text{app}} = S/\dot{\gamma} \) so \( \eta_{\text{app}} = S^{(1-n)/n}K^{1/n} \).

15.6.6 Area of die \( = \pi D^2/4 = 4\pi \text{ cm}^2 \), \( \rho = 900 \text{ kg m}^{-3} \). When \( \dot{\gamma} = 0.0214 \text{ s}^{-1} \) and \( S_w = K \dot{\gamma}^{0.72} \)

\[
S_w = 13400 \times (0.0214)^{0.72} \text{ N m}^{-2} = 841.4 \text{ N m}^{-2}.
\]

\( \dot{\gamma} = 0.0214 = (2V/D)(3 + b) \) where \( b = 1/n = 1/0.072 = 1.389 \)

So \( V = 0.0214 \times 0.04/2 \times 4.389 = 9.752 \times 10^{-5} \text{ m/s} \). So the minimum flow rate \( = \pi D^2 V/4 \text{ m}^3/\text{s} \)

\[
= 1.225 \times 10^{-7} \text{ m}^3/\text{s}.
\]

Mass flow \( = 1.103 \times 10^{-4} \text{ kg/s} = 0.1103 \text{ g/s} \).

For the maximum flow rate \( \dot{\gamma} = 0.427 = 2V \times 4.389/D \). So \( V = 1.946 \times 10^{-3} \text{ m/s} \).

Max flow rate \( = \pi \times 0.02^2 \times 1.946 \times 10^{-3} \text{ m}^3/\text{s} = 2.445 \times 10^{-6} \text{ m}^3/\text{s} \).

Max flow rate \( = 2.2 \times 10^{-3} \text{ kg/s} = 2.2 \text{ g/s} \).

15.6.7 For the Non-Newtonian fluid \( \eta = S_w \dot{\gamma}_w = [S_w/(3+b)]\{D(2V)/8\} \) or \( 4/\eta = [(3+b)V/8D] \).

The approximate viscosity is given by \( \eta_a = S_w 8V/D \) so \( 1/\eta_a = 8V/S_w D \). Then:

\[
\frac{1}{\eta} = \frac{1}{\eta_a} \left( \frac{3}{4} + \frac{b}{4} \right) = \frac{1}{\eta_a} \left( \frac{3}{4} + \frac{1}{4} \frac{d\ln(S_w/\eta)}{d\ln S_w} \right)
\]

But \( \frac{d\ln(S_w/\eta)}{d\ln S_w} = S_w \left( \frac{1}{S_w} - \frac{d\ln S_w}{dS_w} \right) = 1 - \frac{d\ln S_w}{dS_w} \).
So from eqn A, \[ 1/\eta = (1/\eta_\text{a})[1 - (1/4) \frac{d \ln \eta}{d \ln S_\eta}] \]

**Exercises.** 15.9.1 Integrate eqn (15.9.1) to establish eqn (15.9.2).

15.9.2 Establish that the maximum values of \( d \varphi /dr \) occur at \( \varphi_0 = 0 \) and \( \pi \) if \( q < 1 \) (a cigar shaped particle) and at \( \pi/2 \) and \( 3\pi/2 \) if \( q > 1 \) (a disc).

15.9.3 Show that a rigid sphere in Couette flow rotates with a constant velocity equal to half the local shear rate.

15.9.4 Estimate the particle Reynolds number for a system of neutrally buoyant spheres of 100 nm radius suspended in water in a capillary viscometer of length 20 cm, for which the efflux time is 100 seconds. Problems arise in the measurement of viscosity of such systems (due to creation of a particle free zone near the wall) if this Reynolds number exceeds about 10\(^5\). At what particle size does this occur?

**Solutions**

\[ \frac{d \varphi_i}{dt} = \frac{\dot{\gamma}}{q^2 + 1} \left[ \cos^2 \varphi_i + q^2 \sin^2 \varphi_i \right] \]

\[ \int \frac{d \varphi_i}{\cos^2 \varphi_i + q^2 \sin^2 \varphi_i} = \int \frac{\dot{\gamma} \, dr}{q^2 + 1} \]

Dividing through by \( \cos^2 \varphi_i \) on the LHS gives

\[ \int_{r=0}^r \frac{\sec^2 \varphi_i \, d \varphi_i}{1 + q^2 \tan^2 \varphi_i} = \frac{\dot{\gamma} \, t}{q^2 + 1} \]

\[ \frac{1}{q^2} \int \frac{d(q \tan \varphi_i)}{1 + q^2 \tan^2 \varphi_i} = \frac{\dot{\gamma} \, t}{q^2 + 1} \]
\[
\arctan (q \tan \phi) = q \frac{\hat{\gamma}}{(q^2 + 1)} + C \quad \text{and since } \phi = 0 \text{ when } t = 0 \text{ then } C = 0 \text{ so}
\]
\[
\tan \phi = q^{-1} \tan \left( \frac{\hat{\gamma} t}{q + 1/q} \right)
\]

15.92. The maxima and minima in equation 15.9.1 occur when
\[
\frac{d^2 \phi}{dt^2} = -\frac{\hat{\gamma}}{q^2 + 1} \left[ -2 \cos \phi \sin \phi_1 + 2q^2 \sin \phi_1 \cos \phi_1 \right] \frac{d \phi_1}{dt}
\]
\[
= 0 = -\frac{2 \hat{\gamma} (q^2 - 1)}{q^2 + 1} \sin \phi_1 \cos \phi_1 \frac{d \phi_1}{dt}
\]

Now note that \(d \phi_1 / dt \geq 0\) for all \(\phi_1 \geq 0\). Also \(d^2 \phi_1 / dt^2 = 0\) for \(q = 1\) or \(\cos \phi_1 = 0\) or \(\sin \phi_1 = 0\) or \(d \phi_1 / dt = 0\). Thus the minimum in \(d \phi_1 / dt = 0\) and the maxima occur when \(\cos \phi_1 = 0\) or \(\sin \phi_1 = 0\). To show these are maxima we look at
\[
\frac{d \phi}{dt} = \frac{2 \hat{\gamma} (q^2 - 1)}{(q^2 + 1)} \left[ \cos^2 \phi_1 \frac{d \phi_1}{dt} + \sin^2 \phi_1 \frac{d \phi_1}{dt} + \cos \phi_1 \sin \phi_1 \frac{d^2 \phi_1}{dt^2} \right]
\]
\[
= \frac{2 \hat{\gamma} (1 - q^2)}{(q^2 + 1)} \left[ \cos 2\phi_1 \frac{d \phi_1}{dt} + \frac{1}{2} \sin 2\phi_1 \frac{d^2 \phi_1}{dt^2} \right]
\]

When \(q < 1\) this is negative when \(2 \cos 2\phi_1 \frac{d \phi_1}{dt} + \sin 2\phi_1 \frac{d^2 \phi_1}{dt^2} > 0\). For \(\phi_1 = 0\) this is so when \(d \phi_1 / dt > 0\) and this is always so.

For \(\phi_1 = \pi\), \(\sin 2\phi_1 = 0\) and the function is negative when \(2 \cos 2\phi_1 \frac{d \phi_1}{dt} > 0\) and again this is always so. When \(q > 1\) the function \(d \phi / dt^3\) is negative when \(2 \cos 2\phi \frac{d \phi}{dt} + \sin 2\phi \frac{d^2 \phi}{dt^2} < 0\) and for \(\phi = \pi/2\) this is so when \(d \phi / dt > 0\) which again is always so. Likewise for \(\phi = 3\pi/2\).

15.9.3 Using eqn (15.9.1) for a particle of near spherical shape we see that the \(\lim (q - 1) \frac{d \phi}{dt} = (\hat{\gamma}/2)(\cos^2 \phi + \sin^2 \phi) = \hat{\gamma}/2\) and this is the rate of rotation in Couette flow.
15.9.4 The internal (or particle) Reynold's number is \( R^2 \frac{\dot{\gamma} \rho_0}{\eta_0} \) where \( R \) is the radius. Using Table 15.2, the ratio \( \dot{\gamma} \frac{\rho_0}{\eta} = 4Q/\pi a^3 - 8V/D \) where \( V \) is the average fluid velocity = \( Q/\pi a^2 \) and \( D \) is the tube diameter. Taking \( \rho_0 = 10^3 \text{kg m}^{-3} \) for a sphere in water we have (with \( D = 2 \times 10^{-3} \text{m} \)):

\[ R^2 \frac{\dot{\gamma} \rho_0}{\eta_0} = 2 \times 10^{-11} \]. A value of \( 10^{-5} \) would not be reached until \( R \) increased by a factor of about \((10^6/2)^{1/3} = 700\). So for particle sizes greater than about 70 \( \mu \text{m} \) there could be a problem.

**Exercises. 15.10.1** Show that the time taken for a particle of radius \( a \) to undergo Brownian diffusion through a distance equal to its radius is about \( 3\pi \eta a^2/kT \) (refer to Chapter 1.)

15.10.2 Integrate eqn (15.10.10) with \( S = 0 \) when \( \dot{\gamma} = 0 \) to establish eqn (15.10.11) and show how it reduces to eqn (15.2.7). Also show that for substances with a yield value (\( S = S_0 \) when \( \dot{\gamma} = 0 \)) eqn (15.10.10) with \( n = 0 \) integrates to give the equation for Bingham flow.

15.10.3 Establish eqn (15.10.14) by the appropriate integration procedure and determine the conditions under which it yields the equation for the Herschel-Bulkley model.

15.10.4 Use eqns (15.10.21) and (15.10.22) for the Denny and Brodkey model to establish eqn (15.10.23) when \( d\eta/dt = 0 \) and \( n = m = 1 \).

15.10.5 Establish eqn (15.10.26) for the shear modulus. (Note that \( \psi \dot{\gamma}^2 \) is rendered as \( \psi \dot{\gamma} \) in the original paper.)

**Solutions** 15.10.1 \( \langle x^2 \rangle^{1/2} = (2D\dot{\gamma})^{1/2} = a \) (from (1.5.25)) and so \( t = a^2/2D = 3\pi a^2 \eta/kT \).

15.10.2

\[
\int \frac{dS}{(S + \alpha)^n} = \int k^\prime \frac{d\dot{\gamma}}{\left(\dot{\gamma}^\prime + \beta^\prime\right)^n} \quad \text{and for} \quad n < 1
\]

\[
\frac{1}{(n-1)}(S + \alpha)^{-n-1} = \frac{k^\prime}{n-1}\left(\dot{\gamma}^\prime + \beta^\prime\right)^{-n-1} + k_0
\]

S15.17

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So \((S + \alpha)^{n-1} = k' (\dot{\gamma} + \beta)^{n-1} + k_0\) where \(k_0 = k_0 (n-1)\) is an integration constant.

For \(\alpha = \beta = 0\) and \(n = 1\) we have \(\int dS = \int k' d\dot{\gamma}/\dot{\gamma}\) or \(\ln S = k' \ln \dot{\gamma} + k\) and so \(S = K \dot{\gamma}\) where \(n = k'\) and \(\ln K = k_1\).

For \(\alpha \neq 0\) and \(\beta \neq 0\) but \(n = 1\):

\[
\int_0^S \frac{dS}{S + \alpha} = k' \int_0^\dot{\gamma} \frac{d\dot{\gamma}}{\dot{\gamma} + \beta}
\]

and so \(\ln(S + \alpha) = k' [\ln(\dot{\gamma} + \beta)]\)

\(\ln (S + \alpha) - \ln \alpha = k' (\ln [\dot{\gamma} + \beta] - \ln \beta)\) or \(S = \alpha [((\dot{\gamma} + \beta) + \beta)^{k'} - 1]\).

For the Bingham plastic, when \(n = 0\) and \(S = S_B\) when \(\dot{\gamma} = 0\) we have \(\int dS = k' \int \dot{\gamma}\) so \(S - S_B = k' \dot{\gamma}\) which is the Bingham equation.

\[15.10.3\]

\[
\int_0^S \frac{dS}{S + \alpha} = k' \int_0^\dot{\gamma} \frac{d\dot{\gamma}}{\dot{\gamma} + \beta}.
\]

For \(n = 1\) we have:

\[
\left(\frac{\ln(S + \alpha)}{S_B}\right) = k' [\ln(\dot{\gamma} + \beta)]^{\dot{\gamma}}
\]

So \(\ln(S + \alpha) - \ln(S_B + \alpha) = k' \ln(\dot{\gamma} + \beta)\)

\[
\therefore (S + \alpha) = (S_B + \alpha) \left(\frac{\dot{\gamma} + \beta}{\beta}\right)^{k'}
\]

So \(S = (S_B + \alpha) \left(\frac{\dot{\gamma} + \beta}{\beta}\right)^{k'} - 1\) + \(S_B\) \(15.10.4\)
For the Herschel-Bulkley model (eqn 15.2.6) we have $\alpha = 0; \beta << \dot{\gamma}$ and $S_B = S_0$ and $k' = n$.

Then $S = S_0 \dot{\gamma}^n + S_0$ if $[(1 + \beta)/\beta]^{k'} >> 1$ as it will be if $\beta << \dot{\gamma}$.

15.10.4

$$-d\left(\frac{\eta - \eta_0}{\eta_0 - \eta_0}\right)/dr = -\frac{d\eta}{dr} = 0$$

Substituting in eqn(15.10.21) gives:

$$k_1 \left[\frac{\eta_0 - \eta_0}{\eta_0 - \eta_0}\right]^m = k_2 \left[\frac{\eta_0 - \eta_0}{\eta_0 - \eta_0}\right]^m$$

and for $n = m = 1$

$$\frac{\eta - \eta_0}{\eta_0 - \eta} = \frac{k_2}{k_1} = \frac{k_2}{k_1 \dot{\gamma}^p}$$

$$\Rightarrow \frac{\eta - \eta_0}{\eta_0 - \eta} = \frac{k_2}{k_1 \dot{\gamma}^p + k_2} = \left[1 + \frac{k_1 \dot{\gamma}^p}{k_2}\right]^{-1}$$


Now $V_R = (\beta/R) \exp(-\kappa H)$ where $\beta = 4\pi\varepsilon_0\varepsilon_\infty^2 d^2$ 

$$\partial V_R/\partial R = -((\beta/R^2) \exp(-\kappa H) - (\beta\kappa/R) \exp(-\kappa H)$$

since $dR/dH = 1$.

$$\partial^2 V_R/\partial R^2 = (2\beta/R^3) \exp(-\kappa H) + (\beta\kappa/R^2) \exp(-\kappa H) + (\beta\kappa/R^2) \exp(-\kappa H) + (\kappa^2\beta/R) \exp(-\kappa H)$$

$$= (\beta/R^3) \{2 + 2\kappa R + \kappa^2 R^2\} \exp(-\kappa H)$$

from which eqn 15.10.26 follows.