

## 16 Molecular interactions

### 16A Electric properties of molecules

#### Answers to discussion questions

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**16A.2** When the applied field changes direction slowly, the permanent dipole moment has time to reorientate—the whole molecule rotates into a new direction—and follows the field. However, when the frequency of the field is high, a molecule cannot change direction fast enough to follow the change in direction of the applied field and the dipole moment then makes no contribution to the polarization of the sample. Because a molecule takes about 1 ps to turn through about 1 radian in a fluid, the loss of this contribution to the polarization occurs when measurements are made at frequencies greater than about  $10^{11}$  Hz (in the microwave region). We say that the **orientation polarization**, the polarization arising from the permanent dipole moments, is lost at such high frequencies

The next contribution to the polarization to be lost as the frequency is raised is the **distortion polarization**, the polarization that arises from the distortion of the positions of the nuclei by the applied field. The molecule is bent and stretched by the applied field, and the molecular dipole moment changes accordingly. The time taken for a molecule to bend is approximately the inverse of the molecular vibrational frequency, so the distortion polarization disappears when the frequency of the radiation is increased through the infrared. The disappearance of polarization occurs in stages: as shown in Justification 16A.3, each successive stage occurs as the incident frequency rises above the frequency of a particular mode of vibration.

At even higher frequencies, in the visible region, only the electrons are mobile enough to respond to the rapidly changing direction of the applied field. The polarization that remains is now due entirely to the distortion of the electron distribution, and the surviving contribution to the molecular polarizability is called the **electronic polarizability**.

#### Solutions to exercises

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**16A.1(b)** A molecule with a centre of symmetry may not be polar but molecules belonging to the groups  $C_n$ ,  $C_{nv}$ , and  $C_s$  may be polar (Topic 11A).  $\text{SO}_3$ , which has a trigonal planar structure ( $D_{3h}$ ), and  $\text{XeF}_4$ , which is square planar ( $D_{4h}$ ), cannot be polar.  $\boxed{\text{SF}_4}$  (see-saw,  $C_{2v}$ ) may be polar.

$$\begin{aligned} \mathbf{16A.2(b)} \quad \mu_{\text{res}} &= (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{1/2} \quad [16A.3a] \\ &= [(2.5)^2 + (0.50)^2 + (2) \times (2.5) \times (0.50) \times (\cos 120^\circ)]^{1/2} \text{D} = \boxed{2.3 \text{ D}} \end{aligned}$$

$$\begin{aligned} \mathbf{16A.3(b)} \quad \mu &= \sum_i Q_i r_i = 4e(0) - 2er_2 - 2er_3 \quad \text{where} \quad r_2 = \mathbf{i}x_2 \quad \text{and} \quad r_3 = \mathbf{i}x_3 + \mathbf{j}y_3 \\ x_2 &= +162 \text{ pm} \\ x_3 &= r_3 \cos 30^\circ = (+143 \text{ pm}) \times (0.866) = 124 \text{ pm} \\ y_3 &= r_3 \sin 30^\circ = (143 \text{ pm}) \times (0.500) = 71.5 \text{ pm} \end{aligned}$$

The components of the vector sum are the sums of the components.

$$\begin{aligned} \mu_x &= -2ex_2 - 2ex_3 = -2e \times \{(162) + (124)\} \text{ pm} = -e \times (572 \text{ nm}) \\ \mu_y &= -2ey_3 = -2e \times (71.5 \text{ pm}) = -e \times (143 \text{ pm}) \end{aligned}$$

$$\begin{aligned}\mu &= (\mu_x^2 + \mu_y^2)^{1/2} \quad [16A.4b] \\ &= e \times \left\{ (572 \text{ pm})^2 + (143 \text{ pm})^2 \right\}^{1/2} = (1.602 \times 10^{-19} \text{ C}) \times (590 \times 10^{-12} \text{ m}) \\ &= (9.45 \times 10^{-29} \text{ C m}) \times \left( \frac{1 \text{ D}}{3.33564 \times 10^{-30} \text{ C m}} \right) = \boxed{28 \text{ D}}\end{aligned}$$

The angle that  $\mu$  makes with  $x$ -axis is given by

$$\cos \theta = \frac{|\mu_x|}{\mu} = \frac{572}{590} \quad \text{so} \quad \theta = \cos^{-1} \left( \frac{572}{590} \right) = \boxed{14.2^\circ}$$

**16A.4(b)** Polarizability  $\alpha$ , dipole moment  $\mu$ , and molar polarization  $P_m$  are related by

$$P_m = \left( \frac{N_A}{3\epsilon_0} \right) \times \left( \alpha + \frac{\mu^2}{3kT} \right) \quad [16A.12]$$

In order to solve for  $\alpha$ , it is first necessary to obtain  $\mu$  from the temperature variation of  $P_m$ .

$$\alpha + \frac{\mu^2}{3kT} = \frac{3\epsilon_0 P_m}{N_A}$$

Therefore,  $\left( \frac{\mu^2}{3k} \right) \times \left( \frac{1}{T} - \frac{1}{T'} \right) = \left( \frac{3\epsilon_0}{N_A} \right) \times (P_m - P'_m)$  [ $P_m$  at  $T$ ,  $P'_m$  at  $T'$ ]

and hence

$$\begin{aligned}\mu^2 &= \frac{9\epsilon_0 k \times (P_m - P'_m)}{N_A \times \left( \frac{1}{T} - \frac{1}{T'} \right)} \\ &= \frac{9 \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (75.74 - 71.43) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times \left( \frac{1}{320.0 \text{ K}} - \frac{1}{421.7 \text{ K}} \right)} \\ &= 1.045 \times 10^{-59} \text{ C}^2 \text{ m}^2 \\ \mu &= 3.23 \times 10^{-30} \text{ C m} \times \left( \frac{1 \text{ D}}{3.33564 \times 10^{-30} \text{ C m}} \right) = \boxed{0.968 \text{ D}} \\ \alpha &= \frac{3\epsilon_0 P_m}{N_A} - \frac{\mu^2}{3kT} \\ &= \frac{3 \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (75.74 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} - \frac{1.045 \times 10^{-59} \text{ C}^2 \text{ m}^2}{3 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (320.0 \text{ K})} \\ &= \boxed{2.56 \times 10^{-39} \text{ J}^{-1} \text{ C}^2 \text{ m}^2}\end{aligned}$$

Corresponding to  $\alpha' = \frac{\alpha}{4\pi\epsilon_0}$  [16A.6] =  $\boxed{2.29 \times 10^{-29} \text{ m}^3}$

**16A.5(b)**  $M = 85.0 \text{ g mol}^{-1}$

$$\begin{aligned}\epsilon_r - 1 &= \frac{\rho P_m}{M} \times (\epsilon_r + 2) \quad [16A.11] \\ \left( 1 - \frac{\rho P_m}{M} \right) \epsilon_r &= 1 + \frac{2\rho P_m}{M} \\ \epsilon_r &= \frac{M + 2\rho P_m}{M - \rho P_m} \\ &= \frac{85.0 \text{ g mol}^{-1} + 2 \times (1.92 \text{ g cm}^{-3}) \times (32.16 \text{ cm}^3 \text{ mol}^{-1})}{85.0 \text{ g mol}^{-1} - (1.92 \text{ g cm}^{-3}) \times (32.16 \text{ cm}^3 \text{ mol}^{-1})} \\ &= \boxed{8.97}\end{aligned}$$

$$\mathbf{16A.6(b)} \quad n_r = (\epsilon_r)^{1/2} \quad [16A.14] \quad \text{and} \quad \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho N_A \alpha}{3M \epsilon_0} \quad [16A.13]$$

Therefore,

$$\begin{aligned} \alpha &= \frac{3M \epsilon_0 \left( n_r^2 - 1 \right)}{\rho N_A \left( n_r^2 + 2 \right)} \\ &= \frac{3 \times (65.5 \text{ g mol}^{-1}) \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})}{(2.99 \times 10^6 \text{ g m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \times \left( \frac{1.622^2 - 1}{1.622^2 + 2} \right) \\ &= \boxed{3.40 \times 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2} \end{aligned}$$

$$\mathbf{16A.7(b)} \quad \alpha' = \frac{\alpha}{4\pi \epsilon_0} \quad [16A.6]$$

$$\alpha = 4\pi \epsilon_0 \alpha' = (1.11265 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (2.2 \times 10^{-30} \text{ m}^3) = 2.45 \times 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$$

Let

$$C = \frac{\rho N_A \alpha}{3M \epsilon_0} = \frac{(865 \times 10^3 \text{ g m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.45 \times 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2)}{3 \times (72.3 \text{ g mol}^{-1}) \times (8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})} = 0.0665$$

and solve the Clausius–Mossotti eqn [17A.13] for  $\epsilon_r$  with which we calculate the refractive index.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = C \quad [16A.13, \text{ the Clausius – Mossotti eqn}]$$

$$\epsilon_r = \frac{1 + 2C}{1 - C}$$

$$= \frac{1 + 2 \times (0.0665)}{1 - 0.0665}$$

$$= 1.2137$$

$$n_r = \epsilon_r^{1/2} \quad [17.17] = (1.2137)^{1/2} = \boxed{1.10}$$

**16A.8(b)**  $\mu = 5.17 \times 10^{-30} \text{ C m}$  for bromobenzene ( $157.00 \text{ g mol}^{-1}$ )

$$\alpha = 4\pi \epsilon_0 \alpha' \quad [16A.6] = (1.11265 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.5 \times 10^{-29} \text{ m}^3) = 1.67 \times 10^{-39} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$$

$$P_m = \frac{N_A}{3\epsilon_0} \left( \alpha + \frac{\mu^2}{3kT} \right) \quad [16A.12]$$

$$\begin{aligned} &= \frac{6.022 \times 10^{23} \text{ mol}^{-1}}{3 \times (8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})} \left( \frac{(1.67 \times 10^{-39} \text{ J}^{-1} \text{ C}^2 \text{ m}^2)}{+ \frac{(5.17 \times 10^{-30} \text{ C m})^2}{3 \times (1.3807 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}} \right) \\ &= 8.69 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

Let

$$C = \frac{\rho P_m}{M} = \frac{(1.491 \times 10^6 \text{ g m}^{-3}) \times (8.69 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})}{157.00 \text{ g mol}^{-1}} = 0.825$$

and solve the Debye eqn [16A.11] for  $\epsilon_r$ .

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = C \quad [16A.11, \text{ the Debye eqn}]$$

$$\epsilon_r = \frac{1 + 2C}{1 - C}$$

$$= \frac{1 + 2 \times (0.825)}{1 - 0.825}$$

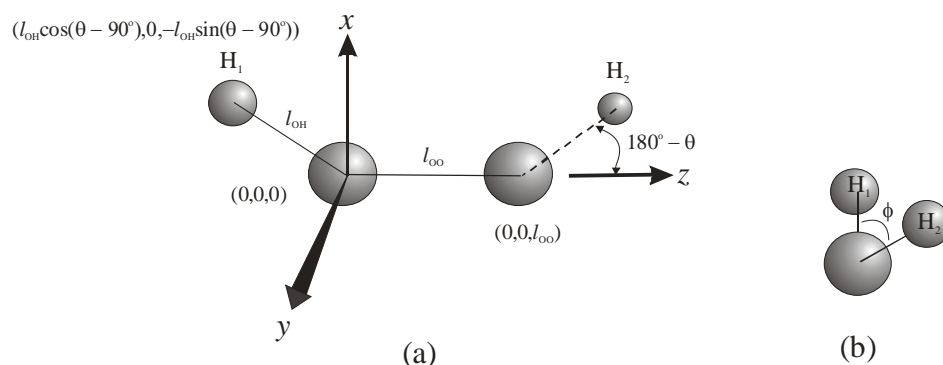
$$= \boxed{15}$$

## Solutions to problems

**16A.2** The point charge model can be used to estimate the magnitude of the electric dipole moment of hydrogen peroxide as a function of  $\phi$  (defined in Fig. 16A.1b as a view down the  $z$  axis of the O–O bond). Each hydrogen atom has a partial charge of  $\delta$ ; each oxygen atom has a partial charge of  $-\delta$ . The dipole moment magnitude is

$$\mu = (\boldsymbol{\mu} \cdot \boldsymbol{\mu})^{1/2} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \text{ where } \mu_x = \sum_j Q_j x_j = \delta \times \{x_{H_1} - x_{O_1} - x_{O_2} + x_{H_2}\} \text{ [16A.4a,b], etc.}$$

We will use the Cartesian coordinate system defined in Fig. 16A.1a. The bond lengths are  $l_{OH} = 97$  pm and  $l_{OO} = 149$  pm. We also use the ratio  $l_{ratio} = l_{OO} / l_{OH} = 1.54$  and calculate  $\mu$  in units of  $\delta l_{OH}$  so that it is unnecessary to estimate the magnitude of  $\delta$ . The O–O–H bond angle,  $\theta$ , may be estimated as  $90^\circ$  but we will use the experimental value of  $100^\circ$ . The computations of  $\mu_x$ ,  $\mu_y$ , and  $\mu_z$  require the coordinates of each atom; those of  $H_1$  and the oxygen atoms are shown in Fig. 16A.1a.



**Figure 16A.1**

The coordinates of  $H_2$  can be determined by analogy to the relationships between Cartesian coordinates and spherical polar coordinates. They are:

$$x = l_{OH} \sin(180^\circ - \theta) \cos \phi$$

$$y = l_{OH} \sin(180^\circ - \theta) \sin \phi$$

$$z = l_{OO} + l_{OH} \cos(180^\circ - \theta)$$

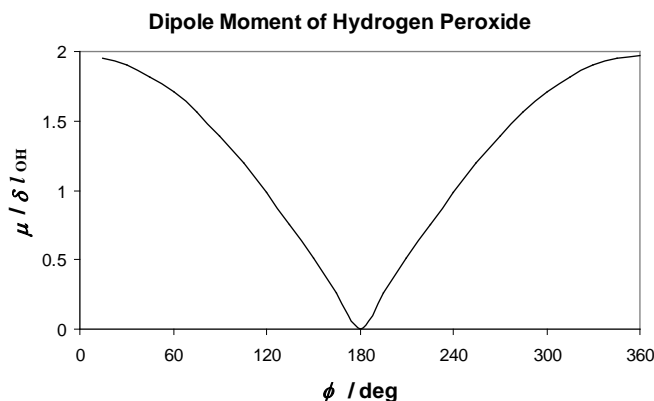
Substitution of variables into eqn. 16A.4b, yields

$$\begin{aligned} (\mu / \delta l_{OH})^2 &= (\mu_x / \delta l_{OH})^2 + (\mu_y / \delta l_{OH})^2 + (\mu_z / \delta l_{OH})^2 \\ &= \{\cos(10^\circ) + \sin(80^\circ) \cos \phi\}^2 + \{\sin(80^\circ) \sin \phi\}^2 + \{-\sin(10^\circ) - l_{ratio} + l_{ratio} + \cos(80^\circ)\}^2 \\ &= \{\cos(10^\circ) + \sin(80^\circ) \cos \phi\}^2 + \{\sin(80^\circ) \sin \phi\}^2 + \{-\sin(10^\circ) + \cos(80^\circ)\}^2 \end{aligned}$$

We now draw a table to calculate  $(\mu / \delta l_{OH})^2$  in  $\phi$  increments of  $15^\circ$  and, subsequently, calculate  $\mu / \delta l_{OH}$  values at each  $\phi$ . Fig. 16A.2 is a plot of the variation. As expected, there the dipole is a maximum of almost twice the single O–H bond dipole when the hydrogen atoms are eclipsed and it is zero when they have a gauche conformation.

$\phi$ / deg	$\phi$ / radians	sq( $\mu / \delta l$ )	$\mu / \delta l$
0	0	3.879385	1.969616
15	0.261799	3.813292	1.952765
30	0.523599	3.619516	1.902502
45	0.785398	3.311262	1.819687
60	1.047198	2.909539	1.705737

Figure 16A.2



16A.4<sup>‡</sup> Let the partial charge on the carbon atom equal  $\delta e$  and the N-to-C distance equal  $l$ . Then,

$$\mu = \delta e l \quad [16A.4a] \quad \text{or} \quad \delta = \frac{\mu}{e l}$$

$$\delta = \frac{(1.77 \text{ D}) \times (3.3356 \times 10^{-30} \text{ C m D}^{-1})}{(1.602 \times 10^{-19} \text{ C}) \times (299 \times 10^{-12} \text{ m})} = \boxed{0.123}$$

16A.6 The induced dipole moment  $\mu^*$  is given by

$$\mu^* = \alpha \mathcal{E} \quad [16A.5a] = 4\pi \epsilon_0 \alpha' \mathcal{E} \quad [16A.6] = \frac{4\pi \epsilon_0 \alpha' e}{4\pi \epsilon_0 r^2} = \frac{\alpha' e}{r^2}$$

Consequently, the dipole-proton distance needed to induce a particular dipole is

$$r = \left( \frac{\alpha' e}{\mu^*} \right)^{1/2}$$

$$= \left( \frac{(1.48 \times 10^{-30} \text{ m}^3) \times (1.602 \times 10^{-19} \text{ C})}{(1.85 \text{ D}) \times (3.336 \times 10^{-30} \text{ C m D}^{-1})} \right)^{1/2} = \boxed{196 \text{ pm}}$$

16A.8  $P_m = \frac{M}{\rho} \times \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right)$  [16A.11] and  $P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9 \epsilon_0 k T}$  [16A.12, with  $\alpha = 4\pi \epsilon_0 \alpha'$ ]

Eqn 16A.12 indicates that, when the permanent dipole moment  $\mu$  contributes to the molar polarization in a manner that is consistent with thermal averaging of the electric dipole moment in the presence of the applied field (i.e., free rotation), a plot of  $P_m$  against  $1/T$  should be linear with an intercept at  $1/T = 0$  equal to  $\frac{4\pi}{3} N_A \alpha'$

and a constant slope for which  $\frac{dP_m}{d(1/T)}$  equals  $\frac{N_A \mu^2}{9 \epsilon_0 k}$ . Eqn 16A.12 is replaced by the Clausius–Mossotti

expression,  $P_m = \frac{4\pi}{3} N_A \alpha'$  [16A.13], in the case for which either the molecules are non-polar or because the

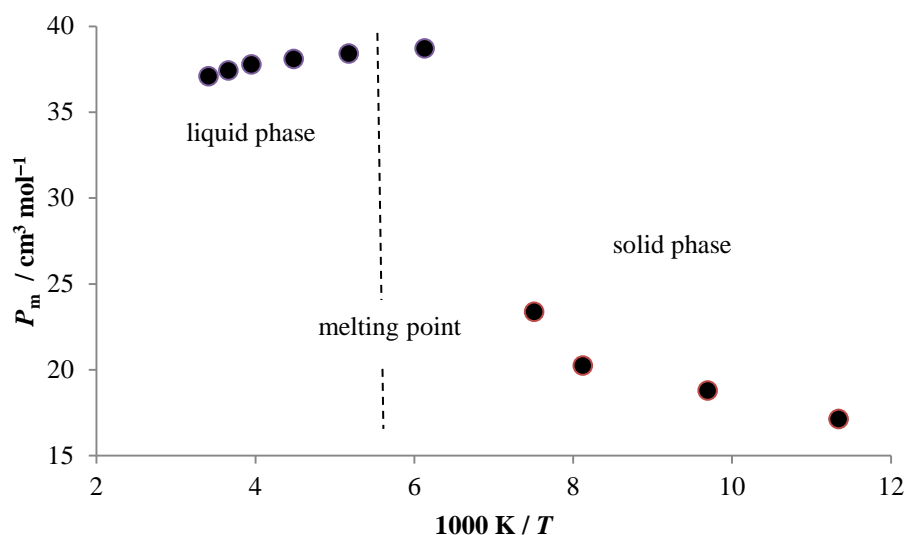
frequency of the applied field is so high that the molecules cannot orientate quickly enough to follow the change in direction of the field.

To examine the possibility that either solid or liquid methanol exhibits the characteristics of eqn 16A.11 or eqn 16A.13, we draw up the following table and prepare the Figure 16A.3 plot of  $P_m$  against  $1/T$ . The molar polarization  $P_m$  is calculated with eqn 16A.11 at all temperatures and, since the data have been corrected for the variation in methanol density, we use  $\rho = 0.791 \text{ g cm}^{-3}$  for all entries and  $M = 32.0 \text{ g mol}^{-1}$ .

<sup>‡</sup>These problems were supplied by Charles Trapp and Carmen Giunta

$\theta / ^\circ\text{C}$	-185	-170	-150	-140	-110	-80	-50	-20	0	20
$T / \text{K}$	88	103	123	133	163	193	223	253	273	293
$\frac{1000}{T / \text{K}}$	11.3	9.69	8.12	7.51	6.13	5.18	4.48	3.95	3.66	3.41
$\epsilon_r$	3.2	3.6	4	5.1	67	57	49	43	38	34
$\frac{\epsilon_r - 1}{\epsilon_r + 2}$	0.42	0.46	0.50	0.58	0.957	0.949	0.941	0.933	0.925	0.917
$\frac{P_m}{(\text{cm}^3 \text{ mol}^{-1})}$	17.1	18.8	20.2	23.4	38.7	38.4	38.1	37.7	37.4	37.1

**Figure 16A.3**



Inspection of Figure 16A.3 reveals that the molar polarization  $P_m$  is not a linear function of  $1/T$  for either the solid or liquid phase of methanol. Nor is it a constant for either phase. Thus, we conclude that the conditions of eqns 16A.12 and 16A.13 are not applicable and it is not possible to extract reliable values for either the polarizability volume or the dipole moment from this data. The data does provide valuable conceptual information about molecular motion in the condensed phases.

Figure 16A.3 indicates that, as the temperature of liquid methanol is reduced,  $P_m$  increases less rapidly than would be expected for the linear case of thermal equilibrium of the dipole with the applied field. The progression toward lower temperatures appears to have a negative second-order component, which extends into the solid phase. The second-order regression fit for  $\theta \leq -110^\circ\text{C}$  reflects this significant non-linearity:

$$P_m / \text{cm}^3 \text{ mol}^{-1} = 31.246 + 2.3788 \times (10^3 \text{ K} / T) - 0.1904 \times (10^3 \text{ K} / T)^2 \quad \text{with } R^2 = 0.9914$$

This indicates that hydrogen-bonding between methanol molecules is hindering molecular rotation and reducing the orientation polarization. The effect extends below the melting point with the  $-110^\circ\text{C}$  data point exhibiting liquid-like, hindered rotation. The large decline of  $P_m$  below  $-110^\circ\text{C}$  is interpreted as corresponding to a stronger hindrance of the dipole moment rotation but the non-constancy of  $P_m$  seems to indicate that rotational excitation is never completely eliminated.

**16A.10** Calculate the dipole moment of  $\text{H}_2\text{O}$  and its polarizability volume.

$$P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\epsilon_0 kT} \quad [16A.12, \text{ with } \alpha = 4\pi\epsilon_0 \alpha']$$

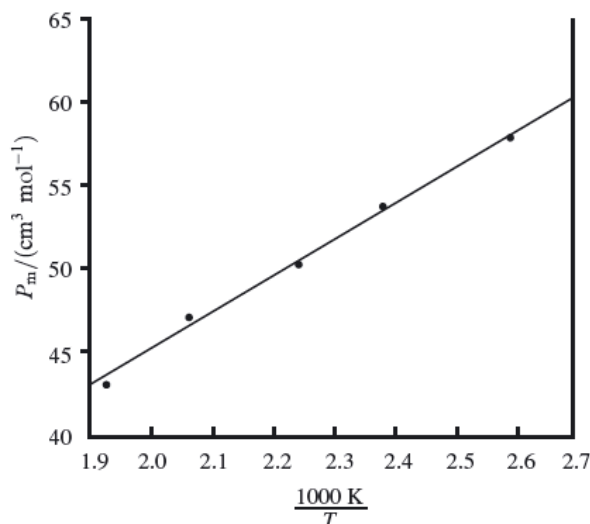
Eqn 16A.12 indicates that a plot of  $P_m$  against  $1/T$  should be linear with a slope,  $\frac{dP_m}{d(1/T)}$ , equal to  $\frac{N_A \mu^2}{9\epsilon_0 k}$  and a

$1/T = 0$  intercept that equals  $\frac{4\pi}{3} N_A \alpha'$ . Therefore, we draw up the following table and prepare a plot of  $P_m$

against  $1/T$ . If it is linear, we perform a linear least squares regression fit of the plot so as to acquire the slope and intercept from which we calculate  $\alpha'$  and  $\mu$ . A suitable plot is shown in Figure 16A.4.

$T/\text{K}$	384.3	420.1	444.7	484.1	522.0
$\frac{1000}{T/\text{K}}$	2.602	2.380	2.249	2.066	1.916
$P_m/(\text{cm}^3 \text{mol}^{-1})$	57.4	53.5	50.1	46.8	43.1

Figure 16A.4



The plot of  $P_m$  against  $1/T$  is linear with a regression fit that gives an intercept of  $3.44 \text{ cm}^3 \text{ mol}^{-1}$  (not shown in the figure), and the slope is such that  $dP_m/d(1/T) = 2.08 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ . It follows that

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{3 \times (3.44 \text{ cm}^3 \text{ mol}^{-1})}{4\pi \times (6.022 \times 10^{23} \text{ mol}^{-1})} = \boxed{1.36 \times 10^{-24} \text{ cm}^3}$$

$$\begin{aligned} \mu^2 &= \frac{9\epsilon_0 k}{N_A} \frac{dP_m}{d(1/T)} \\ &= \left\{ \frac{9 \times (8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.3807 \times 10^{-23} \text{ J K}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right\} \times (2.08 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} \text{ K}) \\ &= 3.80 \times 10^{-59} \text{ C}^2 \text{ m}^2 \\ \mu &= (3.80 \times 10^{-59} \text{ C}^2 \text{ m}^2)^{1/2} \times \left( \frac{1 \text{ D}}{3.33564 \times 10^{-30} \text{ C m}} \right) = \boxed{1.85 \text{ D}} \end{aligned}$$

**16A.12** Since the refractive index  $n_r$  and, therefore, the relative permittivity  $\epsilon_r$  are close to 1, we infer that the dipole moment does not contribute to the molar polarization because either the gas phase molecules are non-polar or the molecular rotational frequency is much lower than the frequency of the applied electric field, which is the case for infrared, visible, and ultraviolet radiation. Furthermore, the observation that the ratio  $C \equiv \frac{\epsilon_r - 1}{\epsilon_r + 2}$

must be much less than 1 greatly simplifies mathematical manipulations.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho N_A \alpha}{3M \epsilon_0} \quad [16A.13, \text{Clausius - Mossotti eqn}] = \frac{\alpha p}{3\epsilon_0 kT} \quad [\rho = Mp / RT, \text{ perfect gas}] \equiv C$$

Solving the Clausius-Mossotti eqn for  $\epsilon_r$  gives

$$\begin{aligned} \epsilon_r &= \frac{1+2C}{1-C} \quad \text{where} \quad C = \frac{\alpha p}{3\epsilon_0 kT} \\ &= (1+2C) \times (1-C+C^2-C^3+\dots) \quad [\text{Taylor series expansion of } (1-C)^{-1} \text{ for } C \ll 1] \\ &= 1+C \quad [\text{Second order and higher powers are insignificantly small and may be discarded.}] \end{aligned}$$

$$\begin{aligned}
n_r &= (1+C)^{1/2} \quad [16A.14] \\
&= 1 + \frac{1}{2}C \quad [\text{Taylor expansion, discard higher order terms}] \\
&= 1 + \frac{\alpha}{6\varepsilon_0 kT} p
\end{aligned}$$

Thus,  $n_r$  is linear in pressure  $p$  with an intercept equal to 1, which corresponds to a vacuum. The slope,  $\frac{\alpha}{6\varepsilon_0 kT}$ , is so small ( $\sim 10^{-4} \text{ bar}^{-1}$ ) that we normally consider the refractive index of a gas to be 1.00. Very sensitive measurements of the refractive index as a function of pressure may be used to find the polarizability. Solving the above equation for  $\alpha$  gives the computational equation using measured values of temperature, pressure, and refractive index:

$$\alpha = 6\varepsilon_0 kT \times (n_r - 1) / p$$

The polarizability volume is calculated with

$$\alpha' = \alpha / 4\pi\varepsilon_0 \quad [16A.6]$$

## 16B Interactions between molecules

### Answers to discussion questions

**16B.2** See Fig. 16A.2 of the text for typical charge arrays corresponding to electric multipoles. As a generality we may write  $V \propto 1/r^{n+m-1}$  [16B.6] for the potential energy of interaction between an  $n$ -pole and an  $m$ -pole. More specifically, the interaction potential between a point charge  $Q_2$  (monopole,  $n = 1$ ) and any of the multipoles ( $m = 2$  or  $3$  or ...) is given as  $V \propto 1/r^m$  where  $r$  is the separation distance between  $Q_2$  and the multipole. This is a steeper potential energy decrease with  $r$  than that observed for the Coulombic interaction between two point charges:  $V \propto 1/r$ . The steeper decline originates in the case for which  $r \gg l$ , where  $l$  is the separation of charge within the multipole, because, as  $r$  becomes relatively large, the array of charges in the multipole appears to blend together into neutrality causing lower order interaction terms to cancel. For example, the dipole terms within the monopole-quadrupole ( $m = 3$ ) interaction potential cancel leaving only a  $1/r^3$  term when  $r \gg l$ .

We use the linear quadrupole charge arrangement shown in Fig. 16B.1 to show this cancellation of lower order terms. Since we are interested in the case  $x = l/r \ll 1$ , the following Taylor series expansions are useful substitutions:

$$(1+x)^{-1} = 1 - x + x^2 - x^3 + \dots \quad \text{and} \quad (1-x)^{-1} = 1 + x + x^2 + x^3 + \dots$$

Begin by adding the terms for the Coulomb potential interaction between the charge array of the quadrupole and the monopole  $Q_2$ , substitute  $x = l/r$ , and perform Taylor series expansions on the functions of  $x$ .

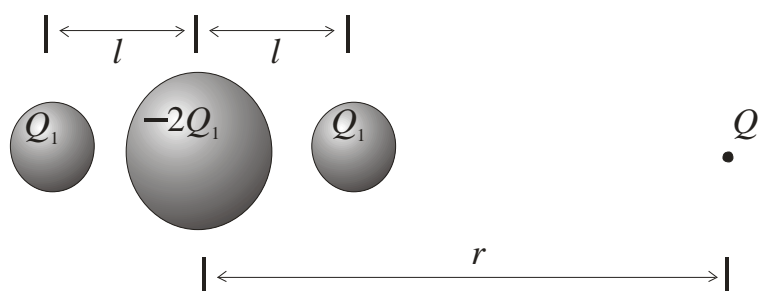
$$\begin{aligned}
4\pi\varepsilon_0 V &= \frac{Q_1 Q_2}{r+l} - \frac{2Q_1 Q_2}{r} + \frac{Q_1 Q_2}{r-l} \\
&= \frac{Q_1 Q_2}{r} \left\{ \frac{1}{1+x} - 2 + \frac{1}{1-x} \right\} \\
&= \frac{Q_1 Q_2}{r} \left\{ \cancel{1} - \cancel{x} + x^2 - x^3 + x^4 + \dots - 2 + 1 + \cancel{x} + x^2 + x^3 + x^4 \dots \right\} \\
&= \frac{2x^2 Q_1 Q_2}{r} \{1 + x^2 + x^4 + \dots\}
\end{aligned}$$

The higher order terms within the polynomial are negligibly small compared to 1 in the case for which  $x = l/r \ll 1$ , thereby, leaving the simple expression:

$$V = \frac{2x^2 Q_1 Q_2}{4\pi\varepsilon_0 r} = \frac{l^2 Q_1 Q_2}{2\pi\varepsilon_0 r^3} \quad \text{or} \quad V \propto \frac{1}{r^3}.$$

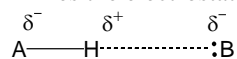


Figure 16B.1



**16B.4 A hydrogen bond** ( $\cdots$ ) is an attractive interaction between two species that arises from a link of the form  $A-H\cdots B$ , where A and B are highly electronegative elements (usually nitrogen, oxygen, or fluorine) and B possesses a lone pair of electrons. It is a contact-like attraction that requires AH to touch B. Experimental evidences supports a linear or near-linear structural arrangement and a bond strength of about  $20 \text{ kJ mol}^{-1}$ . The hydrogen bond strength is considerably weaker than a covalent bond but it is larger than, and dominates, other intermolecular attractions such as dipole-dipole attractions. Its formation can be understood in terms of either the (a) electrostatic interaction model or with (b) molecular orbital calculations.

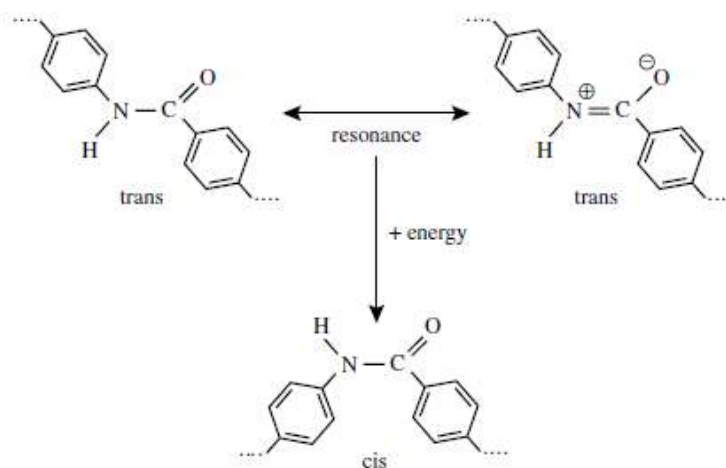
(a) A and B, being highly electronegative, are viewed as having partial negative charges ( $\delta^-$ ) in the electrostatic interaction model of the hydrogen bond. Hydrogen, being less electronegative than A, is viewed as having a partial positive ( $\delta^+$ ). The linear structure maximizes the electrostatic attraction between H and B:



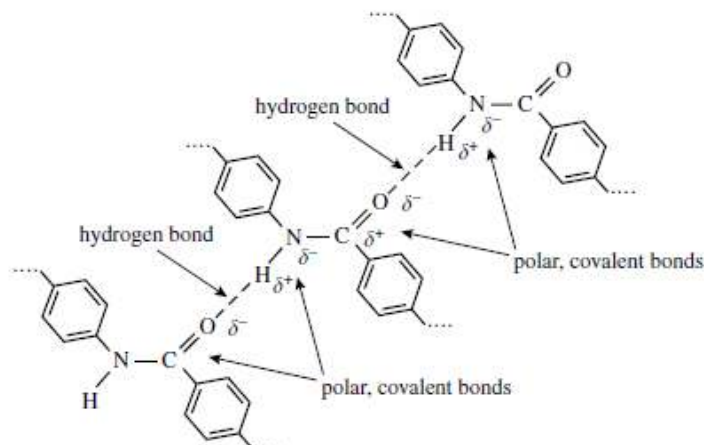
This model is conceptually very useful. However, it is impossible to exactly calculate the interaction strength with this model because the partial atomic charges cannot be precisely defined. There is no way to define which fraction of the electrons of the AB covalent bond should be assigned to one or the other nucleus.

(b) *Ab initio* quantum calculations are needed in order to explore questions about the linear structure, the role of the lone pair, the shape of the potential energy surface, and the extent to which the hydrogen bond has covalent sigma bond character. Yes, the hydrogen bond appears to have some sigma bond character. This was initially suggested by Linus Pauling in the 1930's and more recent experiments with Compton scattering of x-rays and NMR techniques indicate that the covalent character may provide as much as 20% of the hydrogen bond strength. A three-center molecular orbital model provides a degree of insight. A linear combination of an appropriate sigma orbital on A, the  $1s$  hydrogen orbital, and an appropriate orbital for the lone pair on B yields a total of three molecular orbitals. One of the MOs is bonding, one is almost nonbonding, and the third is antibonding. Both bonding MO and the almost nonbonding orbital are occupied by two electrons (the sigma bonding electrons of A-H and the lone pair of B). The antibonding MO is empty. Thus, depending on the precise location of the almost nonbonding orbital, the nonbonding orbital may lower the total energy and account for the hydrogen bond.

**16B.6** Kevlar is a polyaromatic amide. Phenyl groups provide aromaticity and a planar, rigid structure. The amide group is expected to be like the peptide bond that connects amino acid residues within protein molecules. This group is also planar because resonance produces partial double bond character between the carbon and nitrogen atoms. There is a substantial energy barrier preventing free rotation about the CN bond. The two bulky phenyl groups on the ends of an amide group are trans because steric hinderance makes the cis conformation unfavourable.



The flatness of the Kevlar polymeric molecule makes it possible to process the material so that many molecules with parallel alignment form highly ordered, untangled crystal bundles. The alignment makes possible both considerable van der Waals attractions between adjacent molecules and for strong hydrogen bonding between the polar amide groups on adjacent molecules. These bonding forces create the high thermal stability and mechanical strength observed in Kevlar.



Kevlar is able to absorb great quantities of energy, such as the kinetic energy of a speeding bullet, through hydrogen bond breakage and the transition to the cis conformation.

### Solutions to exercises

**16B.1(b)** The H-Cl bond length of a hydrogen chloride molecule is 127.45 pm and the  $\text{Mg}^{2+}$  cation is 300 pm from the dipole center. Because these lengths are comparable, a calculation based on the assumption that the hydrogen chloride dipole acts like a point dipole with a dipole length much shorter than the dipole-ion distance is unlikely to provide an accurate value of the dipole-ion interaction energy. However, such a calculation does provide an "order-of-magnitude" estimate. The minimum value of the dipole-ion interaction occurs with the dipole pointing toward the cation.

$$\begin{aligned}
 V_{\min} &\sim -\frac{\mu_{\text{HCl}} Q_{\text{Mg}^{2+}}}{4\pi\epsilon_0 r^2} \quad [16B.2] = -\frac{2\mu_{\text{HCl}} e}{4\pi\epsilon_0 r^2} \\
 &\sim -\frac{2 \times (1.08 \text{ D}) \times (3.336 \times 10^{-30} \text{ C m D}^{-1}) \times (1.602 \times 10^{-19} \text{ C})}{(1.113 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (300 \times 10^{-12} \text{ m})^2} \\
 &\sim -1.15 \times 10^{-19} \text{ J}
 \end{aligned}$$

The interaction potential becomes a maximum upon flipping the dipole. This effectively changes the sign of the dipole in the previous calculation giving

$$V_{\max} \sim 1.15 \times 10^{-19} \text{ J}$$

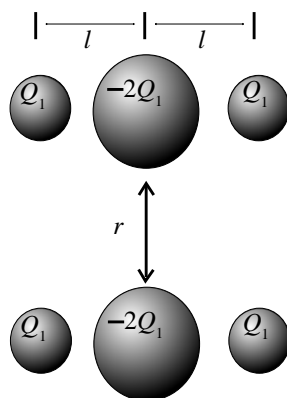
The work  $w$  required to flip the dipole is the difference  $V_{\max} - V_{\min}$ .

$$w \sim V_{\max} - V_{\min} = 2.30 \times 10^{-18} \text{ J}$$

$$w_m = w N_A \sim \boxed{1.39 \times 10^3 \text{ kJ mol}^{-1}}$$

**16B.2(b)** The two linear quadrupoles are shown in Fig. 16B.2 with a parallel configuration.

**Figure 16B.2**



In addition to the distance  $r$  between some of the point charges in one quadrupole and point charges in the other, the Pythagorean theorem provides the distances  $(r^2 + l^2)^{1/2}$  and  $(r^2 + 4l^2)^{1/2}$ . The total potential energy of the interaction between the quadrupoles is:

$$4\pi\epsilon_0 V = \frac{Q_1^2}{r} - \frac{2Q_1^2}{(r^2 + l^2)^{1/2}} + \frac{Q_1^2}{(r^2 + 4l^2)^{1/2}} - \frac{2Q_1^2}{(r^2 + l^2)^{1/2}} + \frac{4Q_1^2}{r}$$

$$- \frac{2Q_1^2}{(r^2 + l^2)^{1/2}} + \frac{Q_1^2}{(r^2 + 4l^2)^{1/2}} - \frac{2Q_1^2}{(r^2 + l^2)^{1/2}} + \frac{Q_1^2}{r}$$

$$\frac{2\pi\epsilon_0 r V}{Q_1^2} = 3 - \frac{4}{(1 + x^2)^{1/2}} + \frac{1}{(1 + 4x^2)^{1/2}} \quad \text{where } x = \frac{l}{r}$$

With the point quadrupole condition that  $x \ll 1$  the last two terms in the above expression can be expanded with the Taylor series:

$$(1 + z)^{-1/2} = 1 - \frac{1}{2}z + \frac{1}{2} \frac{3}{4} z^2 - \frac{1}{2} \frac{3}{4} \frac{5}{6} z^3 + \frac{1}{2} \frac{3}{4} \frac{5}{6} \frac{7}{8} z^4 - \dots$$

$$= 1 - \frac{1}{2}z + \frac{3}{8}z^2 - \frac{15}{48}z^3 + \frac{105}{384}z^4 - \dots$$

where  $z$  is either  $x^2$  or  $4x^2$ .

$$\frac{2\pi\epsilon_0 r V}{Q_1^2} = 3 - 4 \left\{ 1 - \frac{1}{2}x^2 + \frac{3}{8}x^4 - \frac{15}{48}x^6 + \frac{105}{384}x^8 - \dots \right\} + \left\{ 1 - 2x^2 + 6x^4 - 20x^6 + 70x^8 - \dots \right\}$$

$$= -\frac{9}{2}x^4 + \text{higher order terms}$$

In the limit of small  $x$  values the higher order terms are negligibly small, thereby, leaving

$$V = -\frac{9x^4 Q_1^2}{4\pi\epsilon_0 r} = \boxed{-\frac{9l^4 Q_1^2}{4\pi\epsilon_0 r^5}}$$

Thus,  $V \propto \frac{1}{r^5}$  for the quadrupole-quadrupole interaction. See Discussion question 16B.2 and note that a quadrupole is  $n$ -pole array of charges with  $n = 3$ . So the above derivation demonstrates the general potential energy relation between an  $n$ -pole array and an  $m$ -pole array:  $V \propto \frac{1}{r^{n+m-1}} = \frac{1}{r^{3+3-1}} = \frac{1}{r^5}$ .

$$\mathbf{16B.3(b)} V_{\text{London}} = -\frac{3(\alpha'_{\text{Ar}} I_{\text{Ar}})^2}{2(I_{\text{Ar}} + I_{\text{Ar}})r^6} \quad [16B.8] = -\frac{3(\alpha'_{\text{Ar}})^2 I_{\text{Ar}}}{4r^6}$$

$$= -\frac{3 \times (1.66 \times 10^{-30} \text{ m}^3)^2 \times (1520.4 \text{ kJ mol}^{-1})}{4 \times (1.0 \times 10^{-9} \text{ m})^6}$$

$$= \boxed{3.1 \text{ J mol}^{-1}}$$

**16B.4(b)** Using the partial charge presented in the table to the right, we estimate the partial charge on each hydrogen atom of a water molecule to be  $Q_{\text{H}} = \delta e$  where  $\delta = 0.42$ . The electroneutrality of an  $\text{H}_2\text{O}$  molecule implies that the estimated partial charge on the oxygen atom is  $Q_{\text{O}} = -2\delta e$ . With a hydrogen bond length of 170 pm, the point charge model of the hydrogen bond in a continuum of water estimates the potential of interaction to be

$$V = \frac{Q_{\text{H}}Q_{\text{O}}}{4\pi\epsilon r} = -\frac{2(\delta e)^2}{4\pi\epsilon_r\epsilon_0 r} \quad [16B.1]$$

$$= -\frac{2(0.42 \times 1.60 \times 10^{-19} \text{ C})^2}{4\pi(80) \times (8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (170 \times 10^{-12} \text{ m})} = -6.0 \times 10^{-21} \text{ J}$$

<b>Partial charges in polypeptides</b> (from Physical Chemistry; Atkins and de Paula, OUP, 9 <sup>th</sup> ed. 2010)	
Atom	Partial charge / $e$
C(=O)	+0.45
C(-CO)	+0.06
H(-C)	+0.02
H(-N)	+0.18
H(-O)	+0.42
N	-0.36
O	-0.38

The molar energy required to break these bonds is

$$E_{\text{m}} = -N_{\text{A}}V = -(6.022 \times 10^{23} \text{ mol}^{-1}) \times (-6.0 \times 10^{-21} \text{ J}) = \boxed{3.6 \text{ kJ mol}^{-1}}$$

The model of point charges embedded within a continuum of water yields an estimate of the hydrogen bond strength that is well below the experimental value of about  $20 \text{ kJ mol}^{-1}$ . The excessively low estimate has been caused by the assumption that water around the point charges behaves as a continuum of matter. This significantly overestimates the ability of the surrounding water molecules to modulate the point charge interaction.

## Solutions to problems

**16B.2** The positive end of the dipole will lie closer to the (negative) anion in the most energetically favourable orientation for which the anion will be on line with the dipole. Let the positive end of the dipole have a charge  $\delta e$  while the charge on the other end is  $-\delta e$  and the water dipole is defined by  $\mu = \delta e l$ . The electric field generated by a dipole at the distance  $r$  where  $r \gg l$  is sum of the fields generated by these two charges.

$$\mathcal{E} = \frac{\delta e}{4\pi\epsilon_0 \left(r - \frac{l}{2}\right)^2} - \frac{\delta e}{4\pi\epsilon_0 \left(r + \frac{l}{2}\right)^2}$$

$$= \frac{\delta e}{4\pi\epsilon_0 r^2} \left\{ \frac{1}{\left(1 - \frac{l}{2r}\right)^2} - \frac{1}{\left(1 + \frac{l}{2r}\right)^2} \right\}$$

$$= \frac{\delta e}{4\pi\epsilon_0 r^2} \left\{ \left(1 + \frac{l}{r}\right) - \left(1 - \frac{l}{r}\right) \right\} \quad [\text{Taylor series expansion with } \frac{l}{2r} \ll 1.]$$

$$= \frac{\delta e l}{2\pi\epsilon_0 r^3}$$

$$= \frac{\mu}{2\pi\epsilon_0 r^3} \quad [\text{Electric field generated by a point dipole.}]$$

$$= \frac{(1.85 \text{ D}) \times (3.34 \times 10^{-30} \text{ C m D}^{-1})}{2\pi \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times r^3} = \frac{1.11 \times 10^{-19} \text{ V m}^{-1}}{(r / \text{m})^3} = \frac{1.11 \times 10^8 \text{ V m}^{-1}}{(r / \text{nm})^3}$$

(a)  $\mathcal{E} = \boxed{1.1 \times 10^8 \text{ V m}^{-1}}$  when  $r = 1.0 \text{ nm}$

$$(b) \quad \mathcal{E} = \frac{1.11 \times 10^8 \text{ V m}^{-1}}{0.3^3} = \boxed{4 \times 10^9 \text{ V m}^{-1}} \quad \text{for } r = 0.3 \text{ nm}$$

$$(c) \quad \mathcal{E} = \frac{1.11 \times 10^8 \text{ V m}^{-1}}{30^3} = \boxed{4 \text{ kV m}^{-1}} \quad \text{for } r = 30 \text{ nm.}$$

**16B.4 (a)** The energy of induced-dipole–induced-dipole interactions can be approximated by the London formula (eqn. 16B.8):

$$V = -\frac{C}{r^6} = -\frac{3\alpha'_1\alpha'_2}{2r^6} \frac{I_1 I_2}{I_1 + I_2} = -\frac{3\alpha'^2 I}{4r^6}$$

where the second equality uses the fact that the interaction is between two of the same molecule. For two phenyl groups, we have:

$$V = -\frac{3(1.04 \times 10^{-29} \text{ m}^3)^2 \times (5.0 \text{ eV}) \times (1.602 \times 10^{-19} \text{ J eV}^{-1})}{4 \times (4.0 \times 10^{-9} \text{ m})^6} = -1.8 \times 10^{-26} \text{ J or } \boxed{-0.0096 \text{ J mol}^{-1}}$$

Comment. A distance of 0.40 nm, yields  $V = -9.6 \text{ kJ mol}^{-1}$

(b) The potential energy is everywhere negative. We can obtain the distance dependence of the force by taking

$$F = -\frac{dV}{dr} = -\frac{6C}{r^7}.$$

This force is everywhere attractive (i.e., it works against increasing the distance between interacting groups).

The force approaches zero as the distance becomes very large; there is no finite distance at which the dispersion force is zero. (Of course, if one takes into account repulsive forces, then the net force is zero at a distance at which the attractive and repulsive forces balance.)

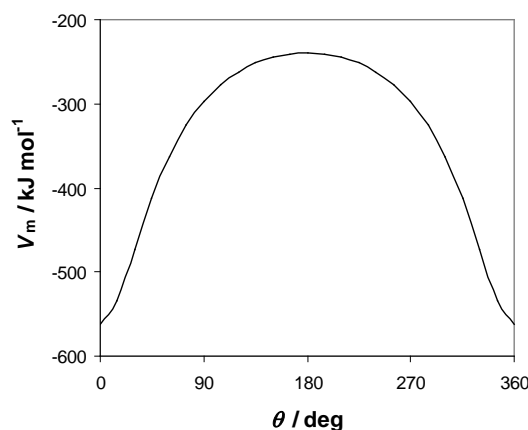
**16B.6** By the law of cosines  $r_{\text{O}\cdots\text{H}}^2 = r_{\text{O-H}}^2 + r_{\text{O-O}}^2 - 2r_{\text{O-H}}r_{\text{O-O}} \cos \theta$ . Therefore,

$$\begin{aligned} r_{\text{O}\cdots\text{H}} &= f(\theta) = (r_{\text{O-H}}^2 + r_{\text{O-O}}^2 - 2r_{\text{O-H}}r_{\text{O-O}} \cos \theta)^{1/2} \\ V_{\text{m}} &= \frac{N_{\text{A}} e^2}{4\pi\epsilon_0} \left\{ \frac{\delta_{\text{O}}\delta_{\text{H}}}{r_{\text{O-H}}} + \frac{\delta_{\text{O}}\delta_{\text{H}}}{r_{\text{O}\cdots\text{H}}} + \frac{\delta_{\text{O-O}}^2}{r_{\text{O-O}}} \right\} = \frac{N_{\text{A}} e^2}{4\pi\epsilon_0} \left\{ \delta_{\text{O}}\delta_{\text{H}} \left( \frac{1}{r_{\text{O-H}}} + \frac{1}{f(\theta)} \right) + \frac{\delta_{\text{O-O}}^2}{r_{\text{O-O}}} \right\} \\ &= \frac{N_{\text{A}} e^2}{4\pi\epsilon_0 \times (10^{-12} \text{ m})} \left\{ \delta_{\text{O}}\delta_{\text{H}} \left( \frac{1}{r_{\text{O-H}}/\text{pm}} + \frac{1}{f(\theta)/\text{pm}} \right) + \frac{\delta_{\text{O-O}}^2}{r_{\text{O-O}}/\text{pm}} \right\} \\ &= (139 \text{ MJ mol}^{-1}) \times \left\{ \delta_{\text{O}}\delta_{\text{H}} \left( \frac{1}{r_{\text{O-H}}/\text{pm}} + \frac{1}{f(\theta)/\text{pm}} \right) + \frac{\delta_{\text{O-O}}^2}{r_{\text{O-O}}/\text{pm}} \right\} \end{aligned}$$

With  $\delta_{\text{O}} = -0.83$ ,  $\delta_{\text{H}} = 0.45$ ,  $r_{\text{O-H}} = 95.7 \text{ pm}$ , and  $r_{\text{O-O}} = 200 \text{ pm}$  we draw up a tabular computation of  $f(\theta)$  and  $V_{\text{m}}(\theta)$  over the range  $0 \leq \theta \leq 2\pi$  and plot  $V_{\text{m}}(\theta)$  in Fig. 16B.3. As expected, the potential is a minimum when  $\theta = 0$  because at that angle the hydrogen lies directly between the two oxygen atoms, which repel.

$\theta / \text{deg}$	$\theta / \text{radian}$	$f(\theta)$	$V / \text{kJ/mol}$
0	0	104.30	-561
15	0.261799	110.38	-534
30	0.523599	126.52	-474
45	0.785398	148.63	-413
60	1.047198	173.26	-363
75	1.308997	198.12	-326
90	1.570796	221.72	-298
105	1.832596	243.04	-277
120	2.094395	261.34	-262
135	2.356194	276.09	-252
150	2.617994	286.90	-245
165	2.879793	293.49	-241
180	3.141593	295.70	-239

Figure 16B.3



**16B.8** The number of molecules in a volume element  $d\tau$  is  $\frac{N d\tau}{V} = \mathcal{N} d\tau$ . The energy of interaction of these molecules with one at a distance  $R$  is  $V(R)\mathcal{N} d\tau$ . The total interaction energy, taking into account the entire sample volume, is therefore

$$u = \int V(R)\mathcal{N} d\tau = \mathcal{N} \int V(R) d\tau \quad [V(R) \text{ is the interaction energy, not the volume}]$$

The total interaction energy of a sample of  $N$  molecules is  $\frac{1}{2}Nu$  (the  $\frac{1}{2}$  is included to avoid double counting), and so the cohesive energy density is

$$v = -\frac{U}{V} = -\frac{\frac{1}{2}Nu}{V} = -\frac{1}{2}\mathcal{N}u = -\frac{1}{2}\mathcal{N}^2 \int V(R) d\tau$$

For  $V(R) = -\frac{C_6}{R^6}$  and  $d\tau = 4\pi R^2 dR$

$$-\frac{U}{V} = 2\pi\mathcal{N}^2 C_6 \int_d^\infty \frac{dR}{R^4} = \frac{2\pi}{3} \times \frac{\mathcal{N}^2 C_6}{d^3}$$

However,  $\mathcal{N} = \frac{N_A \rho}{M}$ , where  $M$  is the molar mass; therefore

$$v = \left( \frac{2\pi}{3} \right) \times \left( \frac{N_A \rho}{M} \right)^2 \times \left( \frac{C_6}{d^3} \right)$$

## 16C Liquids

### Solutions to exercises

**16C.1(b)** Calculate the vapour pressure of a spherical droplet of water of radius 20.0 nm at 35.0 °C. The vapour pressure of bulk water at that temperature is 5.623 kPa and its density is 994.0 kg m<sup>-3</sup>.

$$V_m = \frac{M}{\rho} = \frac{18.02 \text{ g mol}^{-1}}{0.9940 \text{ g cm}^{-3}} = 18.13 \text{ cm}^3$$

$$p = p^* e^{2\gamma V_m(l)/rRT} \quad [16C.20, \text{ the Kelvin eqn}]$$

$$= (5.623 \text{ kPa}) \times \exp \left\{ \frac{2 \times (72.75 \times 10^{-3} \text{ N m}^{-1}) \times (18.13 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}{(20.0 \times 10^{-9} \text{ m}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (308.15 \text{ K})} \right\}$$

$$= \boxed{5.92 \text{ kPa}}$$

**16C.2(b)** The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 30 °C given that at that temperature water climbs to a height of 9.11 cm in a clean glass capillary tube of internal diameter 0.320 mm. The density of water at 30 °C is 0.9956 g cm<sup>-3</sup>.

$$\gamma = \frac{1}{2} \rho g r h \quad [16C.9]$$

$$\begin{aligned}
 &= \frac{1}{2} \times (995.6 \text{ kg m}^{-3}) \times (9.80665 \text{ m s}^{-2}) \times (0.320 \times 10^{-3} \text{ m}) \times (9.11 \times 10^{-2} \text{ m}) \\
 &= 0.142\bar{3} \text{ kg s}^{-2} = \boxed{142 \text{ mN m}^{-1}}
 \end{aligned}$$

**16C.3(b)** Calculate the pressure differential of ethanol across the surface of a spherical droplet of radius 220 nm at 20 °C. The surface tension of ethanol at that temperature is 22.39 mN m<sup>-1</sup>.

$$\begin{aligned}
 p_{\text{in}} - p_{\text{out}} &= \frac{2\gamma}{r} \quad [16C.7, \text{ the Laplace eqn}] \\
 &= \frac{2 \times (22.39 \times 10^{-3} \text{ N m}^{-1})}{220 \times 10^{-9} \text{ m}} \\
 &= 2.04 \times 10^5 \text{ N m}^{-2} = \boxed{204 \text{ kPa}}
 \end{aligned}$$

Pressure differentials for small droplets are quite large.

## Integrated activities

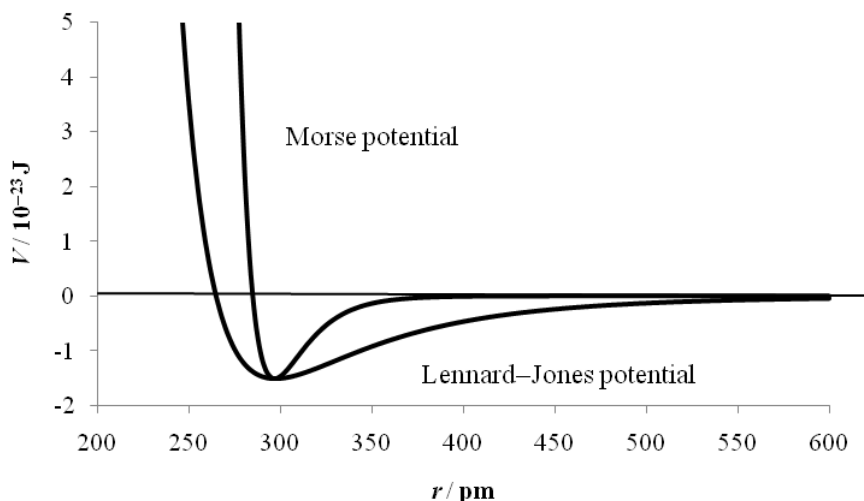
**16.2 (a)**  $V = 4\varepsilon \left\{ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right\}$  [16B.14, Lennard – Jones potential]

The depth of the well in Joules is  $\varepsilon = hc\tilde{D}_e = \boxed{1.51 \times 10^{-23} \text{ J}}$ .

The distance at which the potential is zero is given by

$$r_e = 2^{1/6} r_0 \quad \text{so} \quad r_0 = r_e 2^{-1/6} = 2^{-1/6} \times (297 \text{ pm}) = \boxed{265 \text{ pm}}.$$

A plot of the Lennard-Jones potential is shown in Figure I16.1.



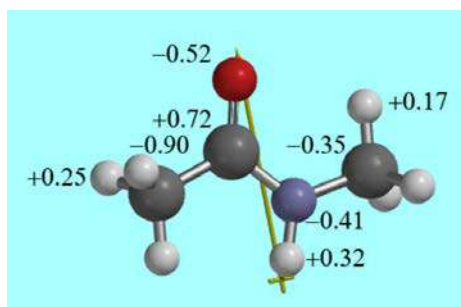
**Figure I16.1**

**(b)**  $V = hc\tilde{D}_e \left\{ 1 - e^{-a(r-r_e)} \right\}^2 - hc\tilde{D}_e$  [12D.11, Morse potential energy]

The constant  $-hc\tilde{D}_e$  has been added to the above expression for the Morse potential so that it has a minimum of  $-hc\tilde{D}_e$  at  $r = r_e$ . This makes it easy to compare the Morse potential with the Lennard–Jones potential of part (a), which also has a minimum of  $-hc\tilde{D}_e$  at  $r = r_e$ . Plots of both potentials are shown in Figure I16.1 with  $a = 0.0579 \text{ pm}^{-1}$  for the Morse potential. The Morse potential has a much steeper repulsive component at separations lower than  $r_e$  while the Lennard–Jones potential shows a longer-range attractive component.

**16.4 (a)** Figure I16.2 displays electrostatic charges on the atoms of trans-*N*-methylacetamide as calculated with the DF/B3LYP/6-31G\* method using Spartan '10 software. The dipole moment vector is shown in the figure

and it approximates points from the positive H atom at the C–H bond to the negative O atom. The calculated dipole moment is  $\mu = 3.64 \text{ D}$ . This agrees well with the experimental dipole moments at  $25^\circ$  of both acetamide (3.6 D, Handbook of Chemistry and Physics, 1991) and trans-*N*-methylacetamide in benzene solution (3.74 D, V.S. Rangra et al, *Z. Naturforsch.*, 61a, 197, 2006).



**Figure I16.2**

The interaction energy of two parallel dipoles is given by eqn. 16B.4:

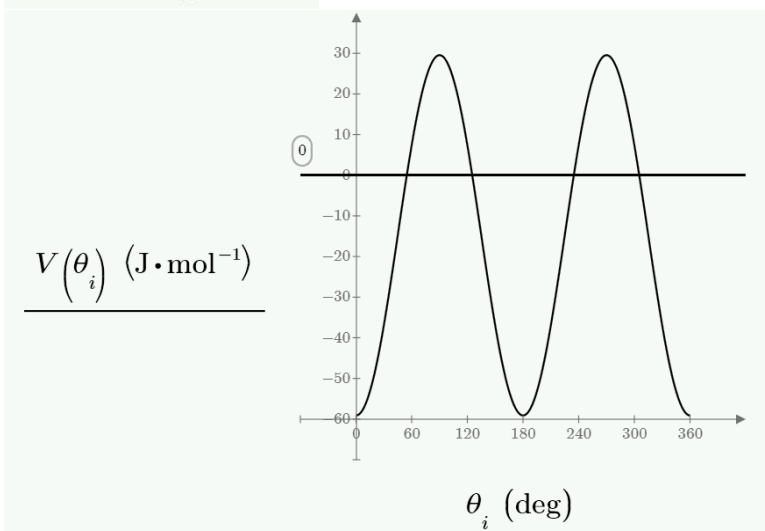
$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\epsilon_0 r^3} \text{ where } f(\theta) = 1 - 3 \cos^2 \theta$$

where  $r$  is the distance between the dipoles and  $\theta$  the angle between the direction of the dipoles and the line that joins them. A plot of the interaction angular dependence is shown in the following Mathcad Prime 2 worksheet. Note that  $V(\theta)$  is at a minimum for  $\theta = 0^\circ$  and  $180^\circ$  while it is at a maximum for  $90^\circ$  and  $270^\circ$ . Furthermore the interaction is positive and repulsive both when  $54.74^\circ < \theta < 125.26^\circ$  and when  $234.74^\circ < \theta < 305.26^\circ$ . Outside these ranges the potential is negative and attractive.

$$\mu := 3.64 \cdot 3.33564 \cdot 10^{-30} \cdot \text{C} \cdot \text{m} \quad r := 3.0 \cdot 10^{-9} \cdot \text{m} \quad \epsilon_0 := 8.85419 \cdot 10^{-12} \cdot \text{J}^{-1} \cdot \text{C}^2 \cdot \text{m}^{-1}$$

$$f(\theta) := 1 - 3 \cdot \cos(\theta)^2 \quad i := 0..360 \quad \theta_i := i \cdot \text{deg} \quad N_A := 6.02214 \cdot 10^{23} \cdot \text{mol}^{-1}$$

$$V(\theta) := \frac{\mu^2 \cdot f(\theta)}{4 \cdot \pi \cdot \epsilon_0 \cdot r^3} \cdot N_A$$



(b)

$$V_{max\_repulsion} := V(90 \cdot \text{deg})$$

$$V_{max\_attraction} := V(180 \cdot \text{deg})$$

$$V_{max\_repulsion} = 0.0296 \text{ kJ} \cdot \text{mol}^{-1}$$

$$V_{max\_attraction} = -0.0591 \text{ kJ} \cdot \text{mol}^{-1}$$

The maximum of both the dipole-dipole repulsion and attraction at 3.0 nm are dwarfed by a hydrogen bond attraction that is typically  $20 \text{ kJ mol}^{-1}$  at about 200 pm. However, the typical hydrogen bond length is much shorter, so this may not be a fair comparison.



**16.6 (a)** Here's a solution using MathCad Prime 2 to perform the bivariable linear model regression fit.  
Data:

$$\log A := [7.36 \ 8.37 \ 8.30 \ 7.47 \ 7.25 \ 6.73 \ 8.52 \ 7.87 \ 7.53]^T$$

$$SW := \begin{bmatrix} 3.53 & 4.24 & 4.09 & 3.45 & 2.96 & 2.89 & 4.39 & 4.03 & 3.80 \\ 1.00 & 1.80 & 1.70 & 1.35 & 1.60 & 1.60 & 1.95 & 1.60 & 1.60 \end{bmatrix}^T$$

The function polyfitc with  $n = 1$  performs the linear fit. The function submatrix takes rows 0-3 and columns 0-2 of polyfitc.

$$\text{Linear\_Regression\_Fit} := \text{submatrix}(\text{polyfitc}(SW, \log A, 1), 0, 3, 0, 2)$$

$$\text{Linear\_Regression\_Fit} = \begin{bmatrix} \text{"Term"} & \text{"Coefficient"} & \text{"Std Error"} \\ \text{"Intercept"} & 3.59 & 0.543 \\ \text{"A"} & 0.957 & 0.152 \\ \text{"B"} & 0.362 & 0.302 \end{bmatrix}$$

Thus, the linear fit is:

$$\log A(S, W) := 3.59 + 0.957 \cdot S + 0.362 \cdot W$$

Value checks give reasonable agreement with the data:

$$\text{Value checks: } \log A(3.53, 1) = 7.33 \quad \log A(2.89, 1.6) = 6.935$$

**(b)** For a group having the properties  $S = 4.84$  and  $\log A = 7.60$ , the linear structure-activity model of part (a) requires the following value of  $W$  if the group is to belong to the set of the data.

$$W = \frac{7.60 - (3.59 + 0.957 \times 4.84)}{0.362}$$

$$= \boxed{-1.72}$$

Clearly, the value  $S = 4.84$  is very much out of the  $S$  data range as is the computed value of  $W$  ( $-1.72$ ) so we expect that a group  $X$ , which has these structure values, does not linearly correlate with this data set. So the question becomes "Can we modify the model so that it meaningfully includes the new group?" Let's try by adding the cross-term  $S \times W$  to the linear model. Here's the Prime 2 worksheet:

$$\text{Linear\_Regression\_Fit} := \text{submatrix}(\text{polyfitc}(SW, \log A, \text{"A B AB"}), 0, 4, 0, 2)$$

$$\text{Linear\_Regression\_Fit} = \begin{bmatrix} \text{"Term"} & \text{"Coefficient"} & \text{"Std Error"} \\ \text{"Intercept"} & 8.728 & 7.133 \\ \text{"A"} & -0.447 & 1.95 \\ \text{"B"} & -2.711 & 4.265 \\ \text{"AB"} & 0.832 & 1.151 \end{bmatrix}$$

$$\log A(S, W) := 8.728 - 0.447 \cdot S - 2.711 \cdot W + 0.832 \cdot S \cdot W$$

$$\text{Value checks: } \log A(3.53, 1) = 7.376 \quad \log A(2.89, 1.6) = 6.946$$

This non-linear structure-activity model seems to adequately describe the groups of part (a) so we now calculate the  $W$  value, using a Mathcad Solve block, for what is an outlier group in the linear model.

log A, S pair:       $\log A := 7.60$        $S := 4.84$

Solver	Guess Values	$W := 1.5$
	Constraints	$\log A = 8.728 - 0.447 \cdot S - 2.711 \cdot W + 0.832 \cdot S \cdot W$
	Solve	$W := \text{Find}(W)$

$W = 0.787$

This is close to the other  $W$  values and it is possible that the cross-term has extended the applicability of the model.