

21 Molecular interactions

Solutions to exercises

Discussion questions

E21.1(b) When the applied field changes direction slowly, the permanent dipole moment has time to reorientate—the whole molecule rotates into a new direction—and follow 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 21.3*, 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.

E21.2(b) There are three van der Waals type interactions that depend upon distance as $1/r^6$; they are the Keesom interaction between rotating permanent dipoles, the permanent-dipole–induced dipole–interaction, and the induced-dipole–induced-dipole, or London dispersion, interaction. In each case, we can visualize the distance dependence of the potential energy as arising from the $1/r^3$ dependence of the field (and hence the magnitude of the induced dipole) and the $1/r^3$ dependence of the potential energy of interaction of the dipoles (either permanent or induced).

E21.3(b) The goal is to construct the radial distribution function, $g(r)$, which gives the relative locations of the particles in the liquid (eqn 21.35). Once $g(r)$ is known it can be used to calculate the thermodynamic properties of the liquid. This expression is nothing more than the Boltzmann distribution of statistical thermodynamics for two molecules in a field generated by all the other molecules in the system.

There are several ways of building the intermolecular potential into the calculation of $g(r)$. Numerical methods take a box of about 10^3 particles (the number increases as computers grow more powerful), and the rest of the liquid is simulated by surrounding the box with replications of the original box (Fig. 21.29 of the text). Then, whenever a particle leaves the box through one of its faces, its image arrives through the opposite face. When calculating the interactions of a molecule in a box, it interacts with all the molecules in the box and all the periodic replications of those molecules and itself in the other boxes. Once $g(r)$ is known it can be used to calculate the thermodynamic properties of liquids.

(a) Monte Carlo methods

In the Monte Carlo method, the particles in the box are moved through small but otherwise random distances, and the change in total potential energy of the N particles in the box, ΔV_N , is calculated

using one of the intermolecular potentials discussed in Sections 21.5 and 21.6. Whether or not this new configuration is accepted is then judged from the following rules:

- 1 If the potential energy is not greater than before the change, then the configuration is accepted.
- 2 If the potential energy is greater than before change, the Boltzmann factor $e^{-\Delta V_N/kT}$ is compared with a random number between 0 and 1; if the factor is larger than the random number, the configuration is accepted; if the factor is not larger, the configuration is rejected. This procedure ensures that at equilibrium the probability of occurrence of any configuration is proportional to the Boltzmann factor. The configurations generated in this way can then be used to construct $g(r)$ simply by counting the number of pairs of particles with a separation r and averaging the result over the whole collection of configurations.

(b) Molecular dynamics

In the molecular dynamics approach, the history of an initial arrangement is followed by calculating the trajectories of all the particles under the influence of the intermolecular potentials. Newton's laws are used to predict where each particle will be after a short time interval (about 1 fs. which is shorter than the average time between collisions), and then the calculation is repeated for tens of thousands of such steps. The time-consuming part of the calculation is the evaluation of the net force on the molecule arising from all the other molecules present in the system.

A molecular dynamics calculation gives a series of snapshots of the liquid, and $g(r)$ can be calculated as before. The temperature of the system is inferred by computing the mean kinetic energy of the particles and using the equipartition result that $\langle 1/2 m v_q^2 \rangle = 1/2 kT$ for each coordinate q .

E21.4(b) Describe how molecular beams are used to investigate intermolecular potentials.

A molecular beam is a narrow stream of molecules with a narrow spread of velocities and, in some cases, in specific internal states or orientations. Molecular beam studies of non-reactive collisions are used to explore the details of intermolecular interactions with a view to determining the shape of the intermolecular potential.

The primary experimental information from a molecular beam experiment is the fraction of the molecules in the incident beam that are scattered into a particular direction. The fraction is normally expressed in terms of dI , the rate at which molecules are scattered into a cone that represents the area covered by the "eye" of the detector (Fig. 21.21 of the text). This rate is reported as the differential scattering cross-section, σ , the constant of proportionality between the value of dI and the intensity, I , of the incident beam, the number density of target molecules, N , and the infinitesimal path length dx through the sample:

$$dI = \sigma IN dx.$$

The value of σ (which has the dimensions of area) depends on the impact parameter, b , the initial perpendicular separation of the paths of the colliding molecules (Fig. 21.22), and the details of the intermolecular potential.

The scattering pattern of real molecules, which are not hard spheres, depends on the details of the intermolecular potential, including the anisotropy that is present when the molecules are non-spherical. The scattering also depends on the relative speed of approach of the two particles: a very fast particle might pass through the interaction region without much deflection, whereas a slower one on the same path might be temporarily captured and undergo considerable deflection (Fig. 21.24). The variation of the scattering cross-section with the relative speed of approach therefore gives information about the strength and range of the intermolecular potential.

Another phenomenon that can occur in certain beams is the capturing of one species by another. The vibrational temperature in supersonic beams is so low that van der Waals molecules may be formed, which are complexes of the form AB in which A and B are held together by van der Waals forces or

hydrogen bonds. Large numbers of such molecules have been studied spectroscopically, including ArHCl, (HCl)₂ArCO₂, and (H₂O)₂. More recently, van der Waals clusters of water molecules have been pursued as far as (H₂O)₆. The study of their spectroscopic properties gives detailed information about the intermolecular potentials involved.

Numerical exercises

E21.5(b) A molecule that has a centre of symmetry cannot be polar. SO₃ (*D*_{3h}) and XeF₄ (*D*_{4h}) cannot be polar. SF₄ (see-saw, *C*_{2v}) may be polar.

E21.6(b) The molar polarization depends on the polarizability through

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

This is a linear equation in T^{-1} with slope

$$m = \frac{N_A \mu^2}{9\epsilon_0 k} \quad \text{so} \quad \mu = \left(\frac{9\epsilon_0 k m}{N_A} \right)^{1/2} = (4.275 \times 10^{-29} \text{ C m}) \times (m / (\text{m}^3 \text{ mol}^{-1} \text{ K}))^{1/2}$$

and with y-intercept

$$b = \frac{N_A \alpha}{3\epsilon_0} \quad \text{so} \quad \alpha = \frac{3\epsilon_0 b}{N_A} = (4.411 \times 10^{-35} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}) b / (\text{m}^3 \text{ mol}^{-1})$$

Since the molar polarization is linearly dependent on T^{-1} , we can obtain the slope m and the intercept b

$$m = \frac{P_{m,2} - P_{m,1}}{T_1^{-1} - T_2^{-1}} = \frac{(75.74 - 71.43) \text{ cm}^3 \text{ mol}^{-1}}{(320.0 \text{ K})^{-1} - (421.7 \text{ K})^{-1}} = 5.72 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$$

$$\begin{aligned} \text{and } b &= P_m - mT^{-1} = 75.74 \text{ cm}^3 \text{ mol}^{-1} - (5.72 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}) \times (320.0 \text{ K})^{-1} \\ &= 57.9 \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

It follows that

$$\mu = (4.275 \times 10^{-29} \text{ C m}) \times (5.72 \times 10^3)^{1/2} = \boxed{3.23 \times 10^{-30} \text{ C m}}$$

$$\text{and } \alpha = (4.411 \times 10^{-35} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}) \times (57.9 \times 10^{-6}) = \boxed{2.55 \times 10^{-39} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}}$$

E21.7(b) The relative permittivity is related to the molar polarization through

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \epsilon_r = \frac{2C + 1}{1 - C},$$

$$C = \frac{(1.92 \text{ g cm}^{-3}) \times (32.16 \text{ cm}^3 \text{ mol}^{-1})}{85.0 \text{ g mol}^{-1}} = 0.726$$

$$\epsilon_r = \frac{2 \times (0.726) + 1}{1 - 0.726} = \boxed{8.97}$$

E21.8(b) If the permanent dipole moment is negligible, the polarizability can be computed from the molar polarization

$$P_m = \frac{N_A \alpha}{3\epsilon_0} \quad \text{so} \quad \alpha = \frac{3\epsilon_0 P_m}{N_A}$$

and the molar polarization from the refractive index

$$\frac{\rho P_m}{M} = \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{n_r^2 - 1}{n_r^2 + 2} \quad \text{so} \quad \alpha = \frac{3\epsilon_0 M}{N_A \rho} \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right)$$

$$\alpha = \frac{3 \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (65.5 \text{ g mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.99 \times 10^6 \text{ g m}^{-3})} \times \left(\frac{1.622^2 - 1}{1.622^2 + 2} \right)$$

$$= \boxed{3.40 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}}$$

E21.9(b) $\mu = qR$ [$q = be$, $b = \text{bond order}$]

For example, $\mu_{\text{ionic}}(\text{C}-\text{F}) = (1.602 \times 10^{-19} \text{ C}) \times (1.41 \times 10^{-10} \text{ m}) = 22.6 \times 10^{-30} \text{ C m} = 6.77 \text{ D}$

Then, per cent ionic character = $\frac{\mu_{\text{obs}}}{\mu_{\text{ionic}}} \times 100$

$\Delta\chi$ values are based on Pauling electronegativities as found in any general chemistry text.

We draw up the following table

Bond	$\mu_{\text{obs}}/\text{D}$	$\mu_{\text{ionic}}/\text{D}$	Per cent	$\Delta\chi$
C—F	1.4	6.77	<input type="text" value="21"/>	1.5
C—O	1.2	6.87	<input type="text" value="17"/>	1.0

The .

Comment. There are other contributions to the observed dipole moment besides the term qR . These are a result of the delocalization of the charge distribution in the bond orbitals.

Question. Is the correlation mentioned in the text [21.2] any better?

E21.10(b) $\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{1/2}$ [21.3a]

$$= [(1.5)^2 + (0.80)^2 + (2) \times (1.5) \times (0.80) \times (\cos 109.5^\circ)]^{1/2} \text{D} = \boxed{1.4 \text{ D}}$$

E21.11(b) The components of the dipole moment vector are

$$\mu_x = \sum_i q_i x_i = (4e) \times (0) + (-2e) \times (162 \text{ pm})$$

$$+ (-2e) \times (143 \text{ pm}) \times (\cos 30^\circ) = (-572 \text{ pm})e$$

$$\text{and } \mu_y = \sum_i q_i y_i = (4e) \times (0) + (-2e) \times (0) + (-2e) \times (143 \text{ pm}) \times (\sin 30^\circ) = (-143 \text{ pm})e$$

The magnitude is

$$\mu = (\mu_x^2 + \mu_y^2)^{1/2} = ((-570)^2 + (-143)^2)^{1/2} \text{ pm } e = (590 \text{ pm})e$$

$$= (590 \times 10^{-12} \text{ m}) \times (1.602 \times 10^{-19} \text{ C}) = \boxed{9.45 \times 10^{-29} \text{ C m}}$$

and the direction is $\theta = \tan^{-1} \frac{\mu_y}{\mu_x} = \tan^{-1} \frac{-143 \text{ pm } e}{-572 \text{ pm } e} = \boxed{194.0^\circ}$ from the x -axis (i.e., 14.0° below the negative x -axis).

E21.12(b) The induced dipole moment is

$$\begin{aligned}\mu^* &= \alpha \mathcal{E} = 4\pi \epsilon_0 \alpha' \mathcal{E} \\ &= 4\pi (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (2.22 \times 10^{-30} \text{ m}^3) \times (15.0 \times 10^3 \text{ V m}^{-1}) \\ &= \boxed{3.71 \times 10^{-36} \text{ C m}}\end{aligned}$$

E21.13(b) The solution to Exercise 21.8(a) showed that

$$\alpha = \left(\frac{3\epsilon_0 M}{\rho N_A} \right) \times \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right) \quad \text{or} \quad \alpha' = \left(\frac{3M}{4\pi \rho N_A} \right) \times \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right)$$

which may be solved for n_r to yield

$$\begin{aligned}n_r &= \left(\frac{\beta' + 2\alpha'}{\beta' - \alpha'} \right)^{1/2} \quad \text{with } \beta' = \frac{3M}{4\pi \rho N_A} \\ \beta' &= \frac{(3) \times (72.3 \text{ g mol}^{-1})}{(4\pi) \times (0.865 \times 10^6 \text{ g m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = 3.31\bar{4} \times 10^{-29} \text{ m}^3 \\ n_r &= \left(\frac{33.1\bar{4} + 2 \times 2.2}{33.1\bar{4} - 2.2} \right)^{1/2} = \boxed{1.10}\end{aligned}$$

E21.14(b) The relative permittivity is related to the molar polarization through

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho P_m}{M} \equiv C \quad \text{so} \quad \epsilon_r = \frac{2C + 1}{1 - C}$$

The molar polarization depends on the polarizability through

$$\begin{aligned}P_m &= \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad \text{so} \quad C = \frac{\rho N_A}{3\epsilon_0 M} \left(4\pi \epsilon_0 \alpha' + \frac{\mu^2}{3kT} \right) \\ C &= \frac{(1491 \text{ kg m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{3(8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (157.01 \times 10^{-3} \text{ kg mol}^{-1})} \\ &\quad \times \left(4\pi (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.5 \times 10^{-29} \text{ m}^3) \right. \\ &\quad \left. + \frac{(5.17 \times 10^{-30} \text{ C m})^2}{3(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \right) \\ C &= 0.83 \quad \text{and} \quad \epsilon_r = \frac{2(0.83) + 1}{1 - 0.83} = \boxed{16}\end{aligned}$$

E21.15(b) The rotation of plane-polarized light is described by

$$\begin{aligned}\Delta\theta &= (n_R - n_L) \frac{2\pi l}{\lambda} \quad \text{so} \quad n_R - n_L = \frac{\lambda \Delta\theta}{2\pi l} \\ &= \left[\frac{(450 \times 10^{-9} \text{ m}) \times (2 \times 192^\circ)}{2\pi (15 \times 10^{-2} \text{ m})} \right] \times \left(\frac{2\pi}{360^\circ} \right) \\ n_R - n_L &= \boxed{3.2 \times 10^{-6}}\end{aligned}$$

Solutions to problems

Solutions to numerical problems

P21.2 The energy of the dipole $-\mu_1 \mathcal{E}$. To flip it over requires a change in energy of $2\mu_1 \mathcal{E}$. This will occur when the energy of interaction of the dipole with the induced dipole of the Ar atom equals $2\mu_1 \mathcal{E}$. The magnitude of the dipole–induced dipole interaction is

$$\begin{aligned}V &= \frac{\mu_1^2 \alpha'_2}{\pi \epsilon_0 r^6} [21.26] = 2\mu_1 \mathcal{E} \text{ [after flipping over]} \\ r^6 &= \frac{\mu_1 \alpha'_2}{2\pi \epsilon_0 \mathcal{E}} = \frac{(6.17 \times 10^{-30} \text{ C m}) \times (1.66 \times 10^{-30} \text{ m}^3)}{(2\pi) \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (1.0 \times 10^3 \text{ V m}^{-1})} \\ &= 1.84 \times 10^{-52} \text{ m}^6 \\ r &= 2.4 \times 10^{-9} \text{ m} = \boxed{2.4 \text{ nm}}\end{aligned}$$

Comment. This distance is about 24 times the radius of the Ar atom.

P21.4 $P_m = \left(\frac{M}{\rho} \right) \times \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right)$ and $P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\epsilon_0 kT}$ [21.15 and 21.16 with $\alpha = 4\pi \epsilon_0 \alpha'$]

The data have been corrected for the variation in methanol density, so use $\rho = 0.791 \text{ g cm}^{-3}$ for all entries. Obtain μ and α' from the liquid range ($\theta > -95^\circ\text{C}$) results, but note that some molecular rotation occurs even below the freezing point (thus the -110°C value is close to the -80°C value). Draw up the following table using $M = 32.0 \text{ g mol}^{-1}$.

$\theta/^\circ\text{C}$	-80	-50	-20	0	20
T/K	193	223	253	273	293
$\frac{1000}{T/\text{K}}$	5.18	4.48	3.95	3.66	3.41
ϵ_r	57	49	42	38	34
$\frac{\epsilon_r - 1}{\epsilon_r + 2}$	0.949	0.941	0.932	0.925	0.917
$P_m/(\text{cm}^3 \text{ mol}^{-1})$	38.4	38.1	37.7	37.4	37.1

P_m is plotted against $\frac{1}{T}$ in Fig. 21.1.

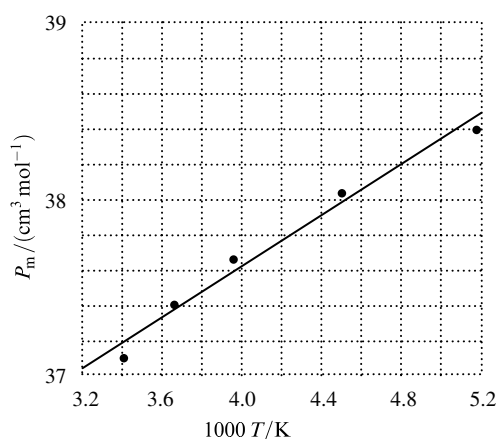


Figure 21.1

The extrapolated intercept at $\frac{1}{T} = 0$ is 34.8 (not shown in the figure) and the slope is 721 (from a least-squares analysis). It follows that

$$\alpha' = \frac{3P_m(\text{at intercept})}{4\pi N_A} = \frac{(3) \times (35.0 \text{ cm}^3 \text{ mol}^{-1})}{(4\pi) \times (6.022 \times 10^{23} \text{ mol}^{-1})} = \boxed{1.38 \times 10^{-23} \text{ cm}^3}$$

$$\mu = (1.282 \times 10^{-2} \text{ D}) \times (721)^{1/2} \text{ [from Problem 21.3]} = \boxed{0.34 \text{ D}}$$

The jump in ϵ_r which occurs below the melting temperature suggests that the molecules can rotate while the sample is still solid.

P21.6

$$P_m = \frac{4\pi}{3} N_A \alpha' + \frac{N_A \mu^2}{9\epsilon_0 kT} \text{ [21.16, with } \alpha = 4\pi \epsilon_0 \alpha']$$

Draw up the following table

T/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

The points are plotted in Fig. 21.2.

The extrapolated (least-squares) intercept is $3.44 \text{ cm}^3 \text{ mol}^{-1}$; the slope is 2.084×10^4 .

$$\mu = (1.282 \times 10^{-2} \text{ D}) \times (\text{slope})^{1/2} \text{ [Problem 21.3]} = \boxed{1.85 \text{ D}}$$

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

Comment. The agreement of the value of μ with Table 22.1 is exact, but the polarizability volumes differ by about 8 per cent.

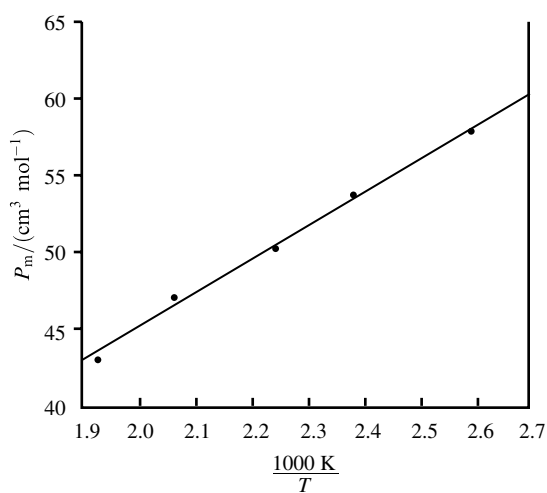


Figure 21.2

P21.7 If there is a simple group-additivity relationship, then α^{elec} ought to be a linear function of the number of Si_2H_4 groups. That is, a plot of α^{elec} versus N ought to be a straight line. The plot is shown in Fig. 21.3 and a table shows values of α^{elec} computed from the best fit of the data and their deviations from the reported values. The equation of the best-fit line is

$$\alpha^{\text{elec}} / (10^{-40} \text{ J}^{-1} \text{ C m}^2) = 4.8008N - 1.7816$$

so the average contribution per Si_2H_4 unit is $4.80 \times 10^{-40} \text{ J}^{-1} \text{ C m}^2$

N	1	2	3	4	5	6	7	8	9
Reported α^{elec}	3.495	7.766	12.40	17.18	22.04	26.92	31.82	36.74	41.63
Best fit α^{elec}	3.019	7.820	12.62	17.42	22.22	27.02	31.82	36.62	41.43
Deviation	0.476	-0.054	-0.22	-0.24	-0.18	-0.098	-0.002	0.110	0.21

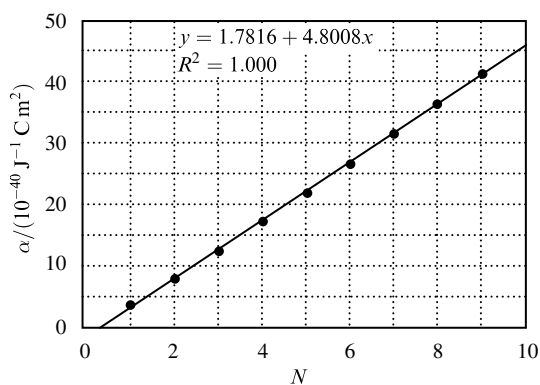


Figure 21.3

The root-mean-square deviation is $0.26 \times 10^{-40} \text{ J}^{-1} \text{ C m}^2$

P21.9 D_0 can be obtained by adding together all the vibrational transitions; then

$$D_e = D_0 + \frac{1}{2} \left(1 - \frac{1}{2}x_e\right) \tilde{\nu} = D_0 + G(0)$$

The potential obviously has some anharmonicity, for no two transitions have the same or nearly the same energy. But we cannot compute x_e without knowing D_e for

$$x_e = \frac{\tilde{\nu}}{4D_e}$$

For that matter, we do not know $\tilde{\nu}$ exactly either. Our best estimate at the moment is $G(1) - G(0)$, which would equal $\tilde{\nu}$ if the vibration were harmonic, but in general it is

$$G(1) - G(0) = \left(1 + \frac{1}{2}\right) \tilde{\nu} - \left(1 + \frac{1}{2}\right)^2 x_e \tilde{\nu} - \left(\frac{1}{2}\tilde{\nu} - \frac{1}{2}x_e \tilde{\nu}\right) = \tilde{\nu}(1 - 2x_e)$$

Our solution is first to compute D_e as if the potential were harmonic, then to compute x_e based on the harmonic D_e and to recompute $\tilde{\nu}$ from $G(1) - G(0)$ and x_e . D_e can then be recomputed based on the improved $\tilde{\nu}$ and x_e and the process repeated until the values stop changing in successive approximations. In the harmonic approximation

$$D_e = 1909.3 + 1060.3 + 386.3 + \frac{1}{2}(1909.3) \text{ m}^{-1} = 4310.6 \text{ m}^{-1}$$

and the parameter a is given by

$$\begin{aligned} a &= \left(\frac{m_{\text{eff}}}{2hcD_e}\right)^{1/2} \omega = \left(\frac{2m_{\text{eff}}c}{hD_e}\right)^{1/2} \pi \tilde{\nu} \\ &= \left(\frac{2(2.2128 \times 10^{-26} \text{ kg}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{(6.626 \times 10^{-34} \text{ J s}) \times (4310.6 \text{ m}^{-1})}\right)^{1/2} \times \pi(1909.3 \text{ m}^{-1}) \\ &= 1.293 \times 10^{10} \text{ m}^{-1} \end{aligned}$$

The anharmonicity constant is substantial

$$x_e = \frac{1909.3 \text{ m}^{-1}}{4(4310.6 \text{ m}^{-1})} = 0.1107$$

A spreadsheet may be used to recompute the parameters, which converge to

$$x_e = 0.1466, \quad \tilde{\nu} = 2701 \text{ m}^{-1}, \quad D_e = 4607 \text{ m}^{-1}, \quad \text{and} \quad a = 1.769 \times 10^{10} \text{ m}^{-1}$$

$$\text{or } D_e = \boxed{46.07 \text{ cm}^{-1}} \text{ and } a = \boxed{1.769 \times 10^8 \text{ cm}^{-1}}$$

P21.11 An electric dipole moment may be considered as charge $+q$ and $-q$ separated by a distance l such that

$$\mu = ql \quad \text{so} \quad q = \mu/l = \frac{(1.77 \text{ D}) \times (3.336 \times 10^{-30} \text{ C m/D})}{299 \times 10^{-12} \text{ m}} = 1.97 \times 10^{-20} \text{ C}$$

In units of the electron charge

$$q/e = (1.97 \times 10^{-20} \text{ C}) / (1.602 \times 10^{-19} \text{ C}) = \boxed{0.123}$$

P21.12 Neglecting the permanent dipole moment contribution

$$\begin{aligned}
 P_m &= \frac{N_A \alpha}{3\epsilon_0} [21.16] \\
 &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (3.59 \times 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2)}{3(8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})} \\
 &= 8.14 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} = \boxed{8.14 \text{ cm}^3 \text{ mol}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \frac{\epsilon_r - 1}{\epsilon_r + 2} &= \frac{\rho P_m}{M} [21.17] \\
 &= \frac{(0.7914 \text{ g cm}^{-3}) \times (8.14 \text{ cm}^3 \text{ mol}^{-1})}{32.04 \text{ g mol}^{-1}} = 0.201
 \end{aligned}$$

$$\epsilon_r - 1 = 0.201\epsilon_r + 0.402; \quad \boxed{\epsilon_r = 1.76}$$

$$n_r = \epsilon_r^{1/2} = (1.76)^{1/2} = \boxed{1.33} [21.19]$$

The neglect of the permanent dipole moment contribution means that the results are applicable only to the case for which the applied field has a much larger frequency than the rotational frequency. Since red light has a frequency of 4.3×10^{14} Hz and a typical rotational frequency is about 1×10^{12} Hz, the results apply in the visible.

Answers to theoretical problems

P21.15 The timescale of the oscillations is about $\frac{1}{0.55 \text{ GHz}} = 2 \times 10^{-9}$ s for benzene and toluene, and 2.5×10^{-9} s for the additional oscillations in toluene. Toluene has a permanent dipole moment; benzene does not. Both have dipole moments induced by fluctuations in the solvent. Both have anisotropic polarizabilities (so that the refractive index is modulated by molecular reorientation). Both benzene and toluene have rotational constants of $\approx 0.2 \text{ cm}^{-1}$, which correspond to the energies of microwaves in this frequency range. Pure rotational absorption can occur for toluene, but not for benzene.

P21.18 An 'exponential-6' Lennard-Jones potential has the form

$$V = 4\epsilon \left[A e^{-r/\sigma} - \left(\frac{\sigma}{r} \right)^6 \right]$$

and is sketched in Fig. 21.4.

The minimum occurs where

$$\frac{dV}{dr} = 4\epsilon \left(\frac{-A}{\sigma} e^{-r/\sigma} + \frac{6\sigma^6}{r^7} \right) = 0$$

which occurs at the solution of

$$\frac{\sigma^7}{r^7} = \frac{A}{6} e^{-r/\sigma}$$

Solve this equation numerically. As an example, when $A = \sigma = 1$, a minimum occurs at $r = \boxed{1.63}$.

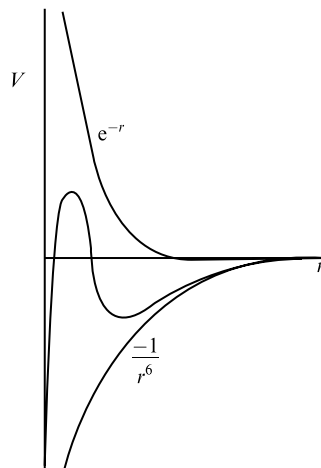


Figure 21.4

P21.19 The number of molecules in a volume element $d\tau$ is $\frac{\mathcal{N} d\tau}{V} = \mathcal{N} d\tau$. The energy of interaction of these molecules with one at a distance r is $\bar{V}\mathcal{N} d\tau$. The total interaction energy, taking into account the entire sample volume, is therefore

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

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

$$\mathcal{U} = -\frac{U}{V} = -\frac{\frac{1}{2}Nu}{V} = -\frac{1}{2}\mathcal{N}u = -\frac{1}{2}\mathcal{N}^2 \int \bar{V} d\tau$$

For $\bar{V} = -\frac{C_6}{r^6}$ and $d\tau = 4\pi r^2 dr$

$$-\frac{U}{V} = 2\pi\mathcal{N}^2 C_6 \int_a^\infty \frac{dr}{r^4} = \frac{2\pi}{3} \times \frac{\mathcal{N}^2 C_6}{d^3}$$

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

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

P21.21 Once again (as in Problem 21.20) we can write

$$\theta(v) = \begin{cases} \pi - 2 \arcsin\left(\frac{b}{R_1 + R_2(v)}\right) & b \leq R_1 + R_2(v) \\ 0 & b > R_1 + R_2(v) \end{cases}$$

but R_2 depends on v

$$R_2(v) = R_2 e^{-v/v^*}$$

Therefore, with $R_1 = \frac{1}{2}R_2$ and $b = \frac{1}{2}R_2$

$$(a) \quad \theta(v) = \pi - 2 \arcsin\left(\frac{1}{1 + 2e^{-v/v^*}}\right)$$

(The restriction $b \leq R_1 + R_2(v)$ transforms into $\frac{1}{2}R_2 \leq \frac{1}{2}R_2 + R_2e^{-v/v^*}$, which is valid for all v .) This function is plotted as curve a in Fig. 21.5.

The kinetic energy of approach is $E = \frac{1}{2}mv^2$, and so

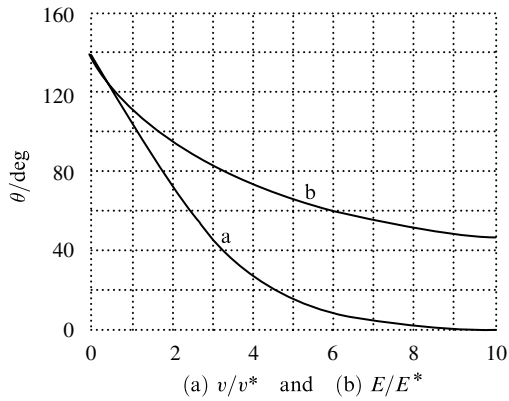


Figure 21.5

$$(b) \quad \theta(E) = \pi - 2 \arcsin\left(\frac{1}{1 + 2e^{-(E/E^*)^{1/2}}}\right)$$

with $E^* = \frac{1}{2}mv^{*2}$. This function is plotted as curve b in Fig. 21.5.