Chapter 9

These are answers to the exercises in Chapter 9 of:

Understanding the Properties of Matter
by Michael de Podesta.

If you find an error in these answers, or think they could be clarified
in any way, please feel free to contact me.

Thanks

Michael@physicsofmatter.com

P1. (a) Selenium, (b) Silicon

C2. There are two approaches that you could take here. The first is to say that the figures are similar to the simulations (which they are) and that this is indicative of the excellent standard of figures throughout the book. This flattery would suffice as an answer. A student with more time might like to print some screenshots and work out the radial density function! This is a lot of work and I have not done it myself but I am confident that you would obtain good results.

To obtain screen shots on a PC
Press the PRINT SCREEN button on the keyboard usually near the top right of the keyboard. This places a bitmap picture of the current screen configuration into the clipboard. Now open an application which can handle such images (WORD will do, but there are many others), and PASTE in the picture which can now be printed.

To obtain screen shots from a Mac
Use the built in help to ask for advice on 'screen shots'. There are several options about printing or saving available but roughly speaking:
- Pressing [Apple] + [shift] + [3] keys simultaneously places a picture file of your whole screen called 'picture 1' on the top level (not the desktop) of your start up disk (usually called Macintosh HD). You should hear a noise like a camera shutter. By the way, you need to press the [3] key on the main keyboard and not on the numeric keypad.
- Pressing [Apple] + [shift] + [4] keys simultaneously places a picture file of a rectangular area of screen called 'picture 1' on the top level (not the desktop) of your start up disk (usually called Macintosh HD). After pressing and releasing the keys, you need to drag the mouse to select the area to be captured. You should hear a noise like a camera shutter. By the way, you need to press the [4] key on the main keyboard and not on the numeric keypad.

P3. All the alcohols have roughly the same density. 805 kg m^{-3} ± 20 kg m^{-3} pretty much covers the range.

For volume V, Density = mass/V = $(0.6V \times \rho_W + 0.4V \times \rho_{Eth})/V$ = 915.6 kg m^{-3}

P4.

We should expect the density of heavy water to be greater than light water by a factor 20/18 = 1.111. The graph below shows the actual data
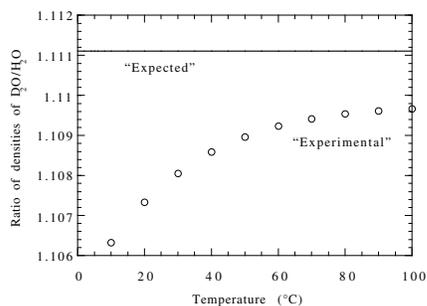
Note that the whole range of the above plot is only ≈ 0.5% of the overall density, so the agreement is pretty good. However the data indicate that the ratio is actually less than we expect. This indicates that either

- Heavy water is less dense than we expected
- Light water is less dense than expected
- A combination of both effects

The fact that there is a significant variation with temperature indicates that there is a structural component to the density differences between light and heavy water. These structural differences are likely to be connected with the different frequencies with which D and H vibrate due to their different masses. There will also be 'quantum' effects connected with the lightness of the hydrogen ions.

2

P5. Mercury: (13600–12860)/13600 = 5.44% decrease in density over 300 °C

i.e. 0.0181% °C^{-1} decrease in density

Recall that for a solid the volume expansivity is just 3 times the linear expansivity so we find:

Gold: $\Delta\rho/\rho = \Delta V/V = 3\times300\times[13\times10^{-6}] = 1.17$ % over 300 °C

i.e. 0.0039% °C^{-1} decrease in density

Gold and mercury are neighbours in the periodic table (Figure 2.2)

P6. Mercury has the highest thermal expansivity

P7. The first key point is that as a body of water is cooled from the air to a temperature less than 4°C, any water at (say) 2 °C is less dense than the water at 4°C at the surface and so the 4°C water sinks to the bottom. Eventually a situation arises where the surface freezes and the water at the bottom is at ≈ 4°C. This is just convection as normally operates in fluids but in this situation (because of the density anomaly) the hotter liquid (4 °C) is denser and sinks whereas more normally the hotter .

The second key point is that ice stays on the surface and does not sink because of the density of ice is less than that of water. If water were 'normal' the ice would sink and the lake would freeze from the bottom up. However the presence of the surface layer of ice very effectively insulates the water, and slows down the freezing process allowing fish and the like to stay alive in liquid throughout prolonged freezing weather.

These two effects conspire keep a volume of unfrozen water at about 4 °C at the bottom of a lake or pool. This allows fish and other aquatic life flora and fauna to survive cold weather without being frozen.

P8. Once the surface freezes over, water in a crack, the liquid inside the crack occupies a volume ≈ 10% too small for ice which it will eventually form i.e. as the ice forms it experiences compressive forces sufficient to reduce its volume by ≈ 10%.

- Assuming a Poisson ratio of 1/2 (not very accurate) , then $\gamma E = B$ (Eq. 9.7) hence if we consider the compression of the liquid then, $B \approx c_L^2 \times \rho \approx 1402^2 \times 1000 \approx 2 \times 10^9$ Pa and hence the pressure is = 2×10^9 Pa $\times 0.1 \approx 2 \times 10^8$ Pa or ≈ 2 kBar.

- Assuming a Poisson ratio of 1/3, then $\gamma \approx 1.5$ hence (Eq 9.3) Hence if we consider the compression of the solid then, $B \approx c_L^2 \times \rho \approx 3800^2 \times 1000 /1.5 \approx 10 \times 10^9$ Pa and hence the pressure is = 10×10^9 Pa $\times 0.1 \approx 10^9$ Pa or ≈ 10 kBar.

These are 'ball park' estimates, but it seems that pressures of the order 1 kBar to 10 kBar seem about right. These are large pressures which can serve to drive open the cracks in a rock.

P9. The speed of sound in the liquids is (a) water 1402 ms^{-1} (b) ethanol 1162 ms^{-1}

P10. (a) Water substance c_{water}/c_{ice} = 0.365   (b) Copper c_{molten}/c_{solid} = 0.704

P11.

Solid Ice, (assuming Poisson ratio $\sigma \approx 1/3$ then $B \approx E$(Eq. A2.33))	Solid Copper (assuming Poisson ratio $\sigma \approx 1/3$ then $B \approx E$(Eq. A2.33))
$B \approx E \approx c_L^2 \times \rho / \gamma \approx 3840^2 \times 920/1.5 = 9.04$ GPa	$B \approx E \approx c_L^2 \times \rho / \gamma \approx 4759^2 \times 8933/1.5 = 134.9$ GPa (Table 7.4 gives 137.8 GPa)
Liquid Water, (assuming Poisson ratio $\sigma \approx 1/2$)	**Liquid copper (assuming Poisson ratio $\sigma \approx 1/2$)**
$B \approx c_L^2 \times \rho \approx 1402^2 \times 1000 = 1.97$ GPa (Table 9.4 gives 2.05 GPa) E has no sensible meaning for liquids	$B \approx c_L^2 \times \rho \approx 3350^2 \times 8000 = 88.9$ GPa E has no sensible meaning for liquids.

Where comparison with tables 7.4 and 9.4 is possible, agreement is very good.

P12. At terminal velocity $(\rho_{sphere} - \rho_{liquid})Vg = 6\pi r\eta v$ and hence $v = (\rho_{sphere} - \rho_{liquid})Vg \,/\, 6\pi r\eta$

Assume spheres $\approx$ 5mm diameter

steel (density $\approx$ 7800 kg m^{-3})

$v = (7800 - 1000)Vg \,/\, 6\pi r\eta$

At 0°C $\dfrac{(7800 - 1000) \times \frac{4}{3}\pi(2.5 \times 10^{-3})^3 \times 9.81}{6\pi \times 2.5 \times 10^{-3} \times 0.0018} = 51.5$ ms^{-1}

At 40°C $\dfrac{(7800 - 1000) \times \frac{4}{3}\pi(2.5 \times 10^{-3})^3 \times 9.81}{6\pi \times 2.5 \times 10^{-3} \times 0.00065} \approx 142$ ms^{-1}

nylon (density $\approx$ 1300 kg m^{-3})

At 0°C $\dfrac{(1300 - 1000) \times \frac{4}{3}\pi(2.5 \times 10^{-3})^3 \times 9.81}{6\pi \times 2.5 \times 10^{-3} \times 0.0018} = 2.27$ ms^{-1}

At 40°C $\dfrac{(1300 - 1000) \times \frac{4}{3}\pi(2.5 \times 10^{-3})^3 \times 9.81}{6\pi \times 2.5 \times 10^{-3} \times 0.00065} \approx 6.29$ ms^{-1}

Even 2.2 m s^{-1} is pretty fast for any kind of hand-timing experiment, and these terminal speeds would only be reached after falling through quite a depth of water (many meters). I can't think how you could carry out a *simple* experiment. If you think of one, please let me know!

P13. Viscosity of water at (a) 0°C $\approx$ 0.0018 Pas (b) 40 °C $\approx$ 0.00065 Pas

Air (density $\approx$ 0.001 kg m^{-3})

At 0°C $v_{\text{terminal}} = \dfrac{(1-1000)\times\frac{4}{3}(0.5\times10^{-3})^2 \times 9.81}{6\times0.0018} = -0.302$ ms^{-1} (minus sign indicates upward motion)
so it takes $\lll$ 0.496 s assuming the bubble travels at terminal velocity for most of its journey.

At 40°C $v_{\text{terminal}} = \dfrac{(1-1000)\times\frac{4}{3}(0.5\times10^{-3})^2 \times 9.81}{6\times0.00065} = -1.373$ ms^{-1} (minus sign indicates upward motion) so it takes $\lll$ 0.109 s assuming the bubble travels at terminal velocity for most of its journey.

The excess pressure under 15 cm of liquid is $\rho gh \approx 1000 \times 9.81 \times 0.15 \approx 1471$ Pa i.e. $\approx 1.47\%$ above ambient pressure. So one would expect the bubble to grow by $\approx 1.47\%$ ($V = nRT/P$), which would not be readily observable

P14.

(a) water at 20 °C $\qquad$ $\gamma = 72.75 \times 10^{-3}$ Nm^{-1} $\qquad$ $\Delta E_S = 43.7$ meV

(b) gold at 1100 °C $\qquad$ $\gamma = 1.1$ Nm^{-1} $\qquad\qquad$ $\Delta E_S = 496$ meV

P15.

(a) copper, $\qquad$ $\approx 3.5 \times 10^2$ Pa

(b) silver, $\qquad$ $\approx 6 \times 10^3$ Pa

(c) gold, $\qquad$ $\approx < 10^2$ Pa

(d) aluminium $\qquad$ $\approx 1.8 \times 10^3$ Pa

P16. To estimate the rate at which molecules leave the surface, we can either estimate the constant A in Eq. 11.8 (by comparing Eq. 11.15 with tabulated values of the vapour pressure in Table 11.6), or note that the rate at which molecules leave the surface will be the same as the rate at which they *would* enter *if* they were in equilibrium with water vapour. Following method 1

At 15°C, Table11.6 tells me that the vapour pressure of water is ≈ 1705 Pa so we find…

$$A \approx \frac{PN_A}{2RTn_L}\exp\left(\frac{\Delta E_e}{k_B T}\right)$$

substituting $\Delta E_e \approx 0.405$ eV and $n_L \approx 3.35 \times 10^{28}$ m^{-3} to find $A \approx 77.2$ (units!) So in Eq. 11.8 we have

$$N_{leaving} \approx \frac{fA}{a^2}\exp\left(\frac{-\Delta E_e}{k_B T}\right) \approx 7.15 \times 10^{26} \text{ molecules s}^{-1}\text{ m}^{-2}$$

This corresponds to a rate of mass loss of $N_{leaving} \times 18\text{u} \approx 21$ kg s^{-1} m^{-2} at 15 °C. This seems a little too high, but if you spill some water outside on a sunny breezy day, then you will find a very high evaporation rate. 10cc of water will spill to make a pool $\approx$ 10cm $\times$ 10 cm $\times$ 1 mm in size which we predict will evaporate at a rate of 0.21 kg s^{-1} i.e. it will evaporate in $\approx$ fraction of second, when in fact it will last for

a few tens of seconds.

P17. If the winds over the sea are not saturated then

$$N_{leaving} \approx \frac{fA}{a^2} \exp\left(-\Delta E_e \big/ k_B T\right) \times 18u \approx 11.1 \text{ kg s}^{-1} \text{ m}^{-2}$$

which corresponds a decline in sea level of the order of 1 cm per second. As discussed in P15, a more realistic estimate may be 1 cm every minute, but it is still fast. It would take $\approx$ 130 days to evaporate the oceans entirely.

Total rate of loss is $\approx 3.8 \times 10^{15}$ kg s^{-1}

P18. Estimate the vapour pressure of water at the boiling temperature of ethanol i.e. 351.5 K =78.35 °C

Using Eq. 11.16 with P = 10^5 and T = 373 K yields an intercept term of 18.692 where we have estimated ΔE_e as L/N_A. Reusing the equation at 351.5 K we find

ln (P/351.5) = 18.692 – (6.74 $\times 10^{-20}$ /(1.38 $\times 10^{-23}$ $\times$ 351.5))

ln (P/351.5) = 18.692 – 13.90 =4.79

Vapour Pressure of water P $\approx$ 42.28 $\times 10^3$ Pa

Vapour Pressure of ethanol $\approx$ 100 $\times 10^3$ Pa i.e. atmospheric pressure.

So roughly speaking, since in the vapour phase pressure is proportional to molar density, the distillate will have water molecules to ethanol molecules in the ratio 42:100 i.e. the distillate will have a minimum of $\approx$ 30% molar concentration of water.

Based on the ratio of vapour pressures, estimate the minimum fraction of water (by molar concentration) that would be present in a distilled water/ethanol mix. By a similar technique estimate the minimum fraction of methanol present. (Equation 11.15 and Table 11.3)

P19. Review the data and explanations presented in §9.4 and 11.3. Write an essay summarising the usefulness of the cell model of a liquid dynamics.

Thermal Properties

P20. (a) water at 0 °C C_P = 75.9 JK^{-1}mol^{-1}

(b) ethanol at 20 °C C_P = 113.4 JK^{-1}mol^{-1}

- For volume V, mass of water is $0.6V \times \rho_W$ so the number of moles of water is

  $0.6V \times \rho_W/0.018 \approx 3.33 \times 10^4 \ V$

- For volume V, mass of ethanol is $0.6V \times \rho_W$ so the number of moles of ethanol is

  $0.4V \times \rho_{ethanol}/0.046 \approx 0.6860 \times 10^4 \ V$

- For V m^3 of vodka, we have

  $3.33 \times 10^4 \ V$ mol of water with heat capacity $\approx$75.9 JK^{-1}mol^{-1} i.e. $2.53 \times 10^6 V$ JK^{-1}

  $0.686 \times 10^4 \ V$ mol of ethanol with heat capacity $\approx$113.4 JK^{-1}mol^{-1} i.e. $0.78 \times 10^6 V$ JK^{-1}

i.e. a total heat capacity per unit volume of $\approx 3.3 \times 10^6$ JK^{-1}m^{-3}. Notice that although there is $\approx$ 50% more water by volume, the water heat capacity contribution is more than three times that of the ethanol.

P21.

(a) water at 20 °C $\kappa = 0.561 + 20 \times (0.673 - 0.561)/(353 - 273)= 0.589$ WK^{-1}m^{-1}

(b) ethanol at 20 °C, $\kappa = 0.189 + 60 \times (0.150 - 0.183)/(353 - 233)=0.1695$ WK^{-1}m^{-1}

Take care: the above examples have 'correction' terms of opposite signs.

(c) mercury at 20 °C C $\kappa \approx 7.8 + 20 \times (9.4 - 7.8)/(373 - 273) \approx 8.1$ WK^{-1}m^{-1}

(d) sodium at 100 °C. $\kappa = 88$ WK^{-1}m^{-1}

P22.

The thermal conductivity of ice is $\approx$ 2.2 W m^{-1} K^{-1} and water is $\approx$ 0.6 W m^{-1} K^{-1} so both are good insulators. If the outside temperature falls to −10 °C then the amount of heat conducted out of the water across the 1 m^2 of frozen ice is $\approx$

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx}$$
$$= -2.2 \times 1 \times \frac{10}{0.01}$$
$$\approx 2200 \ \text{W}$$

5994 J mol

so 1 mol freezes every 5994/2200 = 2.7 seconds 1 mol = 18g = 18 cc

P23. $Q = C_P \times (T_B - T_M)$

	C_P	T_B	T_M	ΔT	M	Q_1 (kJ mol^{-1})	Q_2 (kJ kg^{-1})
water	≈ 76	373	273	100	18	7.6	422
methanol	≈ 81	338	179	159	32	12.9	403
ethanol	≈ 120	352	156	196	46	23.5	511
mercury	28.0	630	234	396	201	11.1	55

P24. The point is in either case (i.e. whether the surface is at 3°C or 5°C) the density of the liquid at the bottom (at 4°C) is greater than the liquid at the surface and there is no convection. So we can use a conventional calculation using the 'still liquid' value of κ.

For water at 4 °C $\kappa = 0.561 + 4 \times (0.673 - 0.561)/(353 - 273) = 0.567$ WK^{-1}m^{-1}

$dQ/dt = 0.567 \times \pi(5 \times 10^{-2})^2 \times (\pm 1)/ 5 \times 10^{-2} \approx \pm 0.089$ W depending on whether the surface is hotter or colder heat flows into or out of the base.

P25. Liquid Density = 930 kg m^{-3} i.e. 40434 mol m^{-3}

(a) 40434 moles of sodium are in the box

(b) First guess is $C_P \approx 3R$ as for a solid, but considering the solid value (≈ 28 JK^{-1} mol^{-1})(Table 7.70) value is probably rather greater than this so guess ≈ 30 JK^{-1} mol^{-1}. So the excess enthalpy in 100 moles 100 °C hotter than its surroundings is $\approx 3 \times 10^5$ J s^{-1} delivered to the top of the box. i.e. convective heat flow is 0.3 MW. Note that 100 moles per second is only 0.25% of the liquid in the box.

The 'still liquid' value for κ is ≈ 80 W K^{-1}m^{-1} so that the heat flow due to conduction is $\approx 80 \times 1 \times 100/1 \approx 8$kW i.e. $\approx$ one fortieth of the convective heat flow.

Electrical Properties

P26. Typographical error: Figure 9.32 incorrectly does not show a factor $\times 10^{-8}$

At 400 °C (673 K), the electrical resistivity of (a) sodium is $\approx 20 \times 10^{-8}$ Ωm^{-1} and (b) potassium is $\approx 32 \times 10^{-8}$ Ωm^{-1}

P27. The Lorentz Number $L = \rho\kappa/T$ which has theoretical value of 2.45×10^{-8} WΩK^{-1} m^{-1}. Sorry.

Using the answer to P24

At 400 °C (673 K), the thermal conductivity of (a) sodium is predicted to be ≈ 82 WK^{-1} m^{-1} (c.f. experimental value ≈ 74 WK^{-1} m^{-1}.)and of (b) potassium is ≈ 51 WK^{-1} m^{-1}. (c.f. experimental value ≈ 42 WK^{-1} m^{-1}.)

P28. $\tau = m_e/(ne^2\rho)$

potassium $\approx 1.6 \times 10^{-14}$ s

8

sodium $\approx 1.5 \times 10^{-14}$ s

Notice that their resistivities differ by a factor of ≈ 1.8

P29. The dielectric constant of (a) water at 20 °C is ≈ 80 (b) ethanol at 20 °C is ≈ 24.3 (c) liquid nitrogen at 70 K is ≈ 1.45

P30.

Optical Properties

P31. At 20 °C, Refractive index of (a) water is 1.33 and of (b) ethanol is 1.314.

For volume V, mass of water is $0.6V \times \rho_W$ so the number of moles of water is

$0.6V \times \rho_W/0.018 \approx 3.33 \times 10^4 \, V$

For volume V, mass of ethanol is $0.6V \times \rho_W$ so the number of moles of ethanol is

$0.4V \times \rho_{ethanol}/0.046 \approx 0.686 \times 10^4 \, V$

i.e. the molar density of water is $3.33/0.686 = 4.85$ times greater than that of ethanol. We would therefore expect that the refractive index would be weighted towards the water value by this factor. So estimate…

$n_{light} \approx (4.85 \times 1.33 + 1 \times 1.314)/5.85 \approx 1.327$

P32. Estimate the refractive index of liquid methanol and liquid ethanol based on the analysis of the water given in the example calculation of Equations 9.51 to 9.56. Compare your results with my calculations in Table 9.20.

	Methanol	Ethanol
Gas Refractive index @ STP	1.000586	1.000878
$n = P/k_BT$	$2.689 \times 10^{25} \text{ m}^{-3}$	$2.689 \times 10^{25} \text{ m}^{-3}$
α	$3.860 \times 10^{-40} \text{ F m}^{-4}$	$5.785 \times 10^{-40} \text{ F m}^{-4}$
$n^{liquid} = N_A\rho/M$	$1.489 \times 10^{28} \text{ m}^{-3}$	$1.033 \times 10^{28} \text{ m}^{-3}$
n_{light} (Predicted byEq.9.45)	1.284	1.294
Experimental	1.329	1.361

P33.

$n = 3.34 \times 10^{28}$ molecules m^{-1}

$\lambda_o \approx 1.6 \times 10^{-7}$ m and $f_o \approx 1.9 \times 10^{15}$ Hz

P34. From Figure 9.35 for water , Refractive index difference for red and blue light is $\approx 1.35\text{-}1.33 = 0.02$ which is a difference of $\approx 1.5\%$

From Figure 7.48 for zinc crown glass, Refractive index difference for red and blue light is $\approx 1.54 - 1.51 = 0.03$ which is a difference of $\approx 2\%$

From Figure 7.48 for light flint glass, Refractive index difference for red and blue light is $\approx 1.62 - 1.57$ =0.05 which is a difference of $\approx 3\%$

So glass is distinctly more dispersive than water.

P35. Basically the refractive index of water is ≈ 1.33 and typical glass has a refractive index ≈ 1.5 so substituting one finds $R \approx 0.004$. whereas light incident upon either water or glass from air.has $R \approx 0.04$ i.e. ≈ 10 times more light is reflected at the interface. Also total internal reflection is reduced, but that is not discussed here.