CHAPTER12

Questions

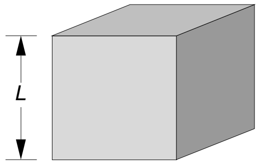
12.1 Introduction

Questions, questions, questions. That is all you will find in this chapter. These questions are more challenging than those found at the end of the chapters, and some questions are completely open-ended! I hope you enjoy them. There are 30 questions: 1 to 10 are mainly about gases; 11 to 13 concern liquids; 14 to 27 are mainly about solids; and questions 27 to 30 concern changes between different phases.

12.2 Gases

1. Buoyancy and the Boltzmann factor

I have always found buoyancy fascinating. It is normally explained with reference to *Archimedes' principle*, and a loose statement that 'less dense objects float'. However, if we consider a helium balloon, or a football held under water, we are familiar with the fact that the object experiences an *upward* force. This can only come from the molecules that surround the object. Recall that gravity can only supply a downward force. This problem looks at the molecular origin of forces of buoyancy.



We will consider a cubic balloon(!) of side L in a medium, say air, of density ρ.

(a) What is the difference in potential energy of a molecule of mass m between the positions at the bottom of the balloon and the top?

(b) What is the relative probability that an individual quantum state will be occupied just above the balloon as compared with just below the balloon? Hint: Look at Example 2.8

(c) What are the relative number densities of molecules just above the balloon as compared with just below the balloon?

(d) If the pressure below the balloon is P_o then write an expression for the pressure above the balloon P in terms of P_o, m, g, L, k_B, and T.

(e) Express the formula in (d) as a linear function of L. To do this you will find it helpful to recall that an exponential function is approximated by $\exp(x) \approx 1 + x$ if $x << 1$.

(f) Using the formula derived in (e), determine the pressure difference between the top of the balloon and the bottom, and so derive a formula for the net upward force. You should find that this exactly reproduces the expression you would have derived if you had equated the upward force to the gravitational force on the mass of the air that the balloon displaced: $\rho L^3 g$.

2.Where is the sky?

When we look up we are familiar with the fact that the sky is blue. Having read §5.8 you will also be familiar with the fact that the colour blue comes from Rayleigh scattering by the molecules of the atmosphere. But where does most of the scattering come from? How high up would you have to go before the sky would look dark?

(a) For a molecule of mass m, what is the difference in the potential energy between being on the ground and being at height h?

(b) What is the relative probability that an individual quantum state will be occupied at the ground and at height h? Hint: Look at Example 2.8

(c) If the number density of molecules at the ground is n_o show that the number density of molecules at height h is given by:

$$n = n_o e^{-mgh/k_B T}$$

(d) The quantity $[k_B T / mg]$ is known as the *scale height*, λ, of the atmosphere. The scale height is the height at which the pressure would fall to $1/e$ of its value at the ground. Evaluate this quantity for the Earth.

(e) Recalling (!) that $\int e^{ax} = \frac{1}{a} e^{ax}$, show that 90% of the molecules in the atmosphere are below a height of approximately 2.3λ. So if we assume that the scattering power of the atmosphere is related to the number of molecules, show that, roughly, the blue of the sky originates at heights below ≈ 20 km.

(f) Do you think the approximation that the atmosphere is at a uniform temperature will seriously affect this result? A graph of mean atmospheric temperature as a function of height (at temperate latitudes) is shown in Question 6. Try comparing your predictions of the variation of number density (and hence pressure, if the temperature is constant) with the following data, which refer to the variation of pressure with height of a 'Standard Atmosphere' of the International Civil Aviation Organisation.

Height (km)	Pressure (kPa)
0	101.3
1	89.9
2	79.5
3	70.1
4	61.6
5	54.0
6	47.2
7	41.1
8	35.6
9	30.7
10	26.4

3. Relative concentrations of O_2 and N_2 at top of Mount Everest

Following on from your calculation of the scale height, λ, of the atmosphere in Question 2, it can be shown that the pressure of an isothermal atmosphere would vary as:

$$P = P_o e^{-mgh/k_B T}$$

where m is the mass of a molecule in the atmosphere, and g is the acceleration due to gravity.

(a) What is the expected pressure of the air at the top of Mount Everest (height $\approx$ 8.9 km)?

(b) Work out the scale heights for oxygen and nitrogen molecules.

(c) Look up the relative concentrations of oxygen and nitrogen in the atmosphere at sea level (Table 5.2) and then work out the ratio of oxygen to nitrogen at top of Mount Everest.

(d) The Yetti are a mysterious and as yet undiscovered species which are believed to inhabit the upper slopes of the Himalayas. They can only live happily in an atmosphere where the air pressure is below 50 kPa. However, their delicate metabolism (which is still a mystery to medical science) also requires that the ratio of oxygen to nitrogen in the atmosphere exceeds 25%. Explain the difficulties that the Yetti face in their ecological niche.

4. Why is there no atmosphere on the Moon?

One can see why there is no atmosphere on the Moon if we compare the typical speeds of gas molecules with the speed necessary to escape the gravitational pull of the Moon, the so-called *escape velocity*. Interestingly, the escape velocity does not depend on the mass of the object trying to 'escape'. It applies equally to a rocket launching a satellite and molecule of a gas.

(a) The gravitational potential energy of an object of mass m at the surface of a planet of mass M and radius R is given by:

$$V = -\frac{GMm}{R}$$

where G is the Newtonian gravitational constant. By equating the magnitude of this energy to the kinetic energy of a particle at the Moon's surface, show that the escape velocity from the Moon is approximately 2380 $\mathrm{ms^{-1}}$.

(b) Imagine that the Moon had an atmosphere of either (i) helium or (ii) nitrogen. For each case, follow Example 4.5 and calculate the fraction of molecules that have speeds greater than the escape velocity. Assume a temperature of 273 K.

Your results for (a) should explain why the Moon has no helium in its atmosphere. Do they explain why the Moon cannot retain an atmosphere of nitrogen? How sensitive are your conclusions to the assumed temperature? What would happen if the average temperature was low, with occasional *very* hot days?

You will probably find the following integrals and values helpful

$$\int_{4.99}^{\infty} x^{\frac{1}{2}} e^{-x}\,\mathrm{d}x \approx 0.017 \qquad \int_{34.9}^{\infty} x^{\frac{1}{2}} e^{-x}\,\mathrm{d}x \approx 10^{-15}$$

$$G = 6.672\times10^{-11}\ \mathrm{m^3\,kg^{-1}\,s^{-2}}$$

$$M_{\mathrm{Earth}} = 5.976\times10^{24}\ \mathrm{kg} \qquad R_{\mathrm{Earth}} = 6371\ \mathrm{km}$$

$$M_{\mathrm{Moon}} = 0.0123\times M_{\mathrm{Earth}} \qquad R_{\mathrm{Moon}} = 0.272\times R_{\mathrm{Earth}}$$

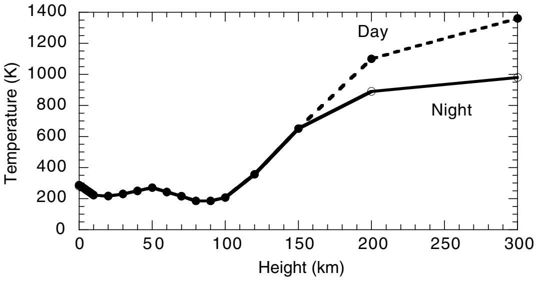
5. Why is there so little helium in the Earth's atmosphere?

There is very little helium in the Earth's atmosphere. For example, at sea level, the concentration of helium is ≈ 5.2 PPM and neon ≈ 18 PPM (*Kaye and Laby*). This is even though helium is constantly being created on the Earth through the α-decay of radioactive elements. So why is there so little helium on Earth? It is tempting, but wrong, to ascribe this to the same reason that the Moon does not have an atmosphere, i.e. that the fast moving tail of the Maxwell–Boltzmann distribution 'leaks' molecules into outer space. That is what I thought until I came to set this and the previous question!

(a) Following the example of the previous question, calculate the fraction of helium molecules which, at 273 K, have speeds greater than the escape velocity of the Earth.

You should find an answer which is *extremely* small. So why is there so little helium in the atmosphere?

(b) Following on from Question 3, work out the scale height λ of an atmosphere composed of helium. This value is greater than for nitrogen by a factor ≈ 7 and indicates that the *relative* concentration of helium increases with increasing height. Thus helium in the atmosphere tends to drift upwards. The temperature of the upper atmosphere increases rapidly above 100 km. This is due to the interactions between molecules and UV- and X-radiation from the Sun: notice the difference between day and night time temperatures. Recalculate your answer from (i) assuming a temperature of 1000 K. Can you understand the loss of helium now?



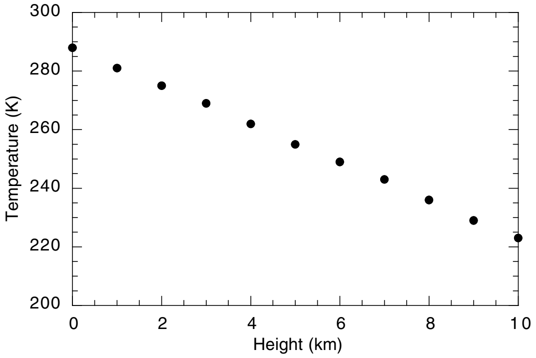
You may find the following values helpful.

$$\int_{110.5}^{\infty} x^{\frac{1}{2}} e^{-x}\,\mathrm{d}x \approx 10^{-47} \qquad \int_{30}^{\infty} x^{\frac{1}{2}} e^{-x}\,\mathrm{d}x \approx 10^{-12}$$

$$M_{\mathrm{Earth}} = 5.976\times10^{24}\ \mathrm{kg} \qquad R_{\mathrm{Earth}} = 6371\ \mathrm{km}$$

6. Stability of the atmosphere against convection

The figure shows the how the mean temperature of the atmosphere changes with height at temperate latitudes. In this question you will attempt (and nobly fail!) to understand why the temperature of the atmosphere falls with height at *just* the rate that it does.



(a) What is the mean temperature gradient in the atmosphere in units of K km^{-1} ?

Consider a volume of gas near the ground. It will rise until its density matches that of the surrounding air. Its volume will adjust to match the surrounding air pressure, but its temperature may differ from that of the surrounding atmosphere. This is because the thermal conductivity of the gas is so poor that over relevant time-scales, the volume of gas is effectively isolated and so it undergoes changes adiabatically rather than isothermally.

(b) For a fixed amount of gas undergoing an isothermal change the quantity $PV = \text{constant}$. For a fixed amount of gas undergoing an adiabatic change the quantity $PV^{\gamma} = \text{constant}$, where $\gamma = C_P/C_V$ is the ratio of the principle specific heats of the gas (See §5.4). Show that for a fixed amount of gas undergoing an adiabatic change the quantity $P^{1-\gamma}T^{\gamma-1} = \text{constant}$, where *constant* has a different value from that in the previous expression.

(c) By first differentiating the expression $P^{1-\gamma}T^{\gamma-1} = \text{constant}$ with respect to height (remembering that both P and T change with height), show that the temperature and pressure gradients in the atmosphere are related by:

$$\frac{\mathrm{d}T}{\mathrm{d}h} = \frac{\gamma-1}{\gamma}\frac{T}{P}\frac{\mathrm{d}P}{\mathrm{d}h}$$

Assuming that atmospheric pressure varies as $P = P_o e^{-mgh/k_BT}$ show that close to the ground the temperature gradient that would develop should be ≈ 9.4 K km^{-1} .

If the temperature gradient is greater than this, volumes of gas at ground level would spontaneously rise because the rapid fall in temperature would make the air above them more dense, 'over-compensating' for the reduction in density due to the falling pressure. (Recall that the density of a gas is given by $\rho = mP/k_BT$). Thus 9.4 K km^{-1} represents the maximum value of temperature gradient sustainable without convection in the Earth's atmosphere. The actual value is smaller than this due to the complicating effect of water vapour.

7. Adiabatic temperature oscillations in a sound wave

The amplitude of pressure oscillations in a sound wave is usually expressed as the ratio of the root mean square (r.m.s.) value of the pressure oscillations to a reference value of $P_o = 2 \times 10^{-5}$ Pa. The ratio is usually expressed logarithmically in units of decibels (dB). Thus the amplitude of sound pressure waves is given by:

$$\text{pressure oscillation amplitude in Pa} = 20\ \log\frac{P_1}{P_o}$$

Thus, for example, if a sound wave had an amplitude of 0.2 Pa, then the pressure oscillation amplitude is 80 dB. This is known technically as the sound pressure level. If the oscillation were at a frequency of 1 kHz, such a sound would be experienced as very loud: equivalent to standing near a road as a large lorry passes.

(a) Starting from $PV^{\gamma} = \text{constant}$, show that $P^{1-\gamma}T^{\gamma} = \text{another constant}$.

(b) For a sound wave travelling through a gas with mean temperature T_o and mean pressure P_o, show that the amplitudes of pressure and temperature oscillations (ΔP and ΔT) are related by:

$$\frac{T_o^{\gamma}}{\left(T_o + \Delta T\right)^{\gamma}} = \frac{P_o^{\gamma-1}}{\left(P_o + \Delta P\right)^{\gamma-1}}$$

(c) When ΔP and ΔT are small compared to P_o and T_o, show that this reduces to:

$$\frac{\Delta T}{T_o} = \frac{(\gamma - 1)}{\gamma}\frac{\Delta P}{P_o}$$

(d) Show that the magnitude of the temperature oscillations associated with an 80 dB sound wave are ≈ 0.16 mK.

(e) How could you detect such tiny rapid temperature oscillations?

8. Diatomic molecules

The covalent bond between the hydrogen and the chlorine in a HCl molecule has a 'spring constant' of $K = 860\ \text{Nm}^{-1}$.

(a) Assuming that the chlorine atom is heavy enough for it to scarcely vibrate at all, calculate the resonant frequency of oscillation of the hydrogen atom.

(b) How many degrees of freedom should you expect this gas to exhibit at around room temperature?

(c) Estimate the temperature above which you should expect this gas to show a heat capacity of $C_P = 37.4\ \text{J K}^{-1}\ \text{mol}^{-1}$.

(d) Help! My poor graduate student has confused two flasks. One contains HCl and the other contains and equal number of moles of DCl. Remember deuterium is the name for the heavy isotope of hydrogen D = ^{2}H. Its bonding to chlorine is identical to ordinary hydrogen, but of course it has twice the mass. I casually suggest that HCl and DCl can easily be distinguished at certain temperatures by the difference in their heat capacity. Can you suggest a good temperature range in which to try this experiment? Which gas would have the higher heat capacity in this range?

(e) I then remember that it would probably be easier to distinguish between the gases by measuring the speed of sound through the gases. Which would have the higher speed of sound? And how big would you expect the difference to be?

(f) Can you think of another (even simpler?) way to distinguish between the two gases?

9. My office.

The office in which I used to work was 5 m long by 4m wide and an amazing 5m high! It had a mean temperature of around 23 °C. Assume that the air is composed entirely of nitrogen and oxygen in the ratio 4:1.

(a) Calculate the total *translational* energy of the air molecules in my room.

(b) In order to stay cool, my colleague Dr. Zochowski and I used a fan. This device gives an excess velocity of ≈ 2 ms^{-1} to approximately 0.5 m^3 of air per second. After the coherent directed velocity of the air has turned into random molecular motions, the temperature of the air in the room will rise slightly. Calculate the power input to the room from the fan.

(c) Calculate the rate of temperature rise in the room due to the fan. (Neglect convection and assume that the temperature of the room is uniform.)

(d) Write a paragraph explaining to one of your less scientific friends why a device which actually heats the room makes me feel cooler!

(e) The cooling effect of the fan is related to the so called 'wind chill' effect. But is it always a 'chill' effect? Explain how using a fan when defrosting a refrigerator would provide a 'wind heating' effect.

(f) In summer my office heats up to around 28 °C, but in winter the temperature falls to around 18 °C. How many molecules of oxygen are there in the room in winter? How many more (or is it how many fewer?) molecules of oxygen are there in summer?

(g) My lung capacity is around 2.5 litres, but when I relax, I generally inhale only around 0.5 litres of air in each breath. In each breath I use around 20% of the available oxygen in my lungs, expelling the rest. If my office were sealed so that no air could enter or leave, and I were alone (without even e-mail!), estimate how long I would survive. When the oxygen fraction in the room falls below around 15% I will become unconscious, and when it falls below 10% I will expire. 'Tell me the truth now… how long have I got?'

10. The virial equation

The ideal gas equation accurately describes the properties of nearly all gases in a wide variety of situations. However, if you want to be very careful indeed you can use the virial equation (Equation 4.50) to take account of deviations from ideal gas behaviour. This is written as:

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B(T)}{V_\mathrm{m}} + \frac{C(T)}{V_\mathrm{m}^2} + \ldots \qquad (1)$$

where V_m is the molar volume. We can write the second virial coefficient $B(T)$ as:

$$B(T) = a - b\exp\left[\frac{c}{T}\right] \qquad (2)$$

We can use Equations 1 and 2 to decide when deviations from ideal gas behaviour exceed 1%, i.e. when the second term on the right-hand side of Equation 1 exceeds 0.01.

(a) Explain why, if we are looking only for small deviations from ideal gas behaviour, we may write the right-hand side of the virial equation as:

$$1 + \frac{B(T)P}{RT}$$

(b) Using data in the table below, sketch the function $B(T)$ for nitrogen across the range in which the above formula is valid.

(c) Using data in the table below, estimate the *temperature* below which (at atmospheric pressure) the deviations from ideal gas behaviour are such that the second term in Equation 3 exceeds 0.01. (This needs to done numerically)

(d) Consider the temperatures calculated in (c) as a fraction of the boiling temperature of the appropriate liquid. Is there a pattern?

(e) For each of the gases in the table, estimate the mean separation between atoms when the deviations exceed 1%. Comment on your results.

				a, b and c valid	
Gas	***a*** **m³ mol⁻¹**	***b*** **m³ mol⁻¹**	***c*** **K**	***From*** **(K)**	***To*** **(K)**
Helium	114.1	98.7	3.245	7	150
Neon	81.0	63.6	30.7	44	973
Argon	154.2	119.3	105.1	80	1024
Krypton	189.6	148.0	145.3	110	700
Xenon	247.0	192.9	199.8	160	650
Water	33.0	15.2	1300.7	293	1248
Nitrogen	185.4	141.8	88.7	75	700
Oxygen	152.8	117.0	108.8	90	400

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Liquids

11. Van der Waals equation of state

The Van der Waals (VdW) Equation of state for z moles is mentioned briefly in §4.5.2 as a development of the ideal gas equation. The equation for z moles of substance is given by (*c.f.* Equation 4.44):

$$\left[P + \frac{z^2 a}{V^2}\right][V - zb] = zRT \qquad (1)$$

Equation 1 is in fact a good deal more interesting than just a modification to the ideal gas law. Amazingly – at least *I* find it amazing – this equation not only describes the small deviations from ideal gas behaviour, but also allows a fair description of the liquid state! However, working analytically with Equation 1 is considerably more complicated than the ideal gas equation.

(a) For nitrogen the parameters a and b are given by $a = 0.1408$ m^3 Pa mol^{-1} and $b = 3.913 \times 10^{-5}$ m^3 mol^{-1}. Use a spreadsheet or graph-plotting program to plot the predicted graphs of P versus V for temperatures of 200 K, 130 K, 120 K and 100 K for $z = 1$ mol. Remember that b is (roughly speaking) the volume of 1 mole of the substance in the solid state. So plot V from say $1.1b$ to say $100b$ in suitably small steps. You will need to use a logarithmic scale on both axes to see clearly the behaviour of the $P(V)$ across this range. On the same graph plot the predicted behaviour using the ideal gas equation.

(b) The VdW graph at 200 K should look like an ideal gas at all volumes except that it is distorted so that the zero of volume corresponds to a volume of b. Explain briefly why this is so.

(c) The VdW graphs at 120 and 130 K should show a distinct kink. This is close to the critical temperature T_C of nitrogen. Recall that above T_C nitrogen can not be liquefied at any pressure. *At* the critical temperature the graph should have a point of inflection but not a minimum. Based on these graphs estimate the critical volume and pressure and compare your estimates with the data in Table 11.4.

(d) At 100 K, the graph shows a distinct kink with a maxima and minima. (This is unphysical: d*P*/d*V* is positive and if you think about it that cannot be right.) This region is discussed in many texts (e.g. *Flowers and Mendoza*) but the usual approach is to ignore it! The wiggle in this region corresponds roughly to the region in which liquid and gas co-exist. At volumes well below the kink region, the equation describes the properties of a liquid modestly well. Estimate the compressibility of a liquid from the slope of your curve at around $V = 1.1b$. Following the discussion in §9.3, state briefly whether or not you consider this estimate to be reasonably accurate.

(e) If you still have not had enough, then compare the experimental and predicted critical temperatures for:

- Argon:
  $a = 0.1362$ m^3 Pa mol^{-1} and
  $b = 3.219\times10^{-5}$ m^3 mol^{-1},
- CO$_2$:
  $a = 0.3639$ m^3 Pa mol^{-1} and
  $b = 4.267\times10^{-5}$ m^3 mol^{-1}.

12. Radial density function of two-dimensional fluid

This question concerns a two-dimensional fluid, similar to that discussed at the start of Chapter 8 in Example 8.1. The 'molecules' of the fluid are, for the purposes of this calculation, impenetrable discs with radius $r_o = 1.1 \times 10^{-9}$ m.

(a) If the molecules are in a low-density gas-like phase with a number density *n* per unit area, sketch the radial distribution function *g*(*r*) and radial density function ρ(*r*).

(b) The molecules interact via a pair potential with the form:

$$u_{\text{pair}}(r) = \frac{-5\times10^{-83}}{r^6}\ \text{J} \quad \text{if } r \geq 2r_o$$

and at 600 K the molecules are in a gas-like phase and occupy an area ten times greater than the total area of the discs themselves. Estimate (i) the molar internal potential energy using:

$$U = \frac{N_A}{2}\int_0^\infty g(r)u_{\text{pair}}(r)\text{d}r$$

and (ii) the molar internal kinetic energy assuming that the molecules exhibit two degrees of freedom. By comparing the results of (i) and (ii), comment on the validity of the assumption that the molecules are in a gas-like phase.

(c) At a lower temperature the radial distribution function has the form:

$$g(r) = 0 \quad \text{for} \quad r < 2r_o$$
$$g(r) = 3Cr \quad \text{for} \quad 2r_o \leq r < 4r_o$$
$$g(r) = Cr \quad \text{for} \quad 4r_o \leq r < 5r_o$$
$$g(r) = 2Cr \quad \text{for} \quad r \geq 5r_o$$

where *C* has the value 2×10^{18} m^{-2}. Sketch the radial distribution function *g*(*r*) and radial density function *ρ*(*r*).

(d) Evaluate the molar internal potential energy using formula given in (b).

13. Radial density function of three-dimensional liquid

The radial distribution function *N*(*r*) in the liquid phase of the newly invented element *Hypotheticum* is shown below. The constant *C* has the value 1.5×10^{29} m^{-3}. The molecules of hypotheticum have a relative molecular mass of 70 and are perfectly spherical hard spheres, with a weak force of attraction between atoms.

(a) From the form of *N*(*r*) estimate the diameter r_o of an atom of Hypotheticum.

(b) Sketch a graph of the radial *density* function and so estimate the density of liquid hypotheticum at this temperature and pressure.

(c) The pair-potential function for these molecules is given by:

$$u_{\text{pair}}(r) = -1.6\times10^{-22}\ \text{J}\ \text{ if }\ 3r_{\text{o}} \le r < 6r_{\text{o}}$$

Sketch $u_{\text{pair}}(r)$ and then estimate the depth of the attractive potential expressed in kelvin.

$$u_{\text{pair}}(r) = -1.6\times10^{-22}\ \text{J}\ \text{ if }\ 3r_{\text{o}} \le r < 6r_{\text{o}}$$

Sketch $u_{\text{pair}}(r)$ and then estimate the depth of the attractive potential expressed in kelvin.

(d) Show that the contribution of the molecular interaction to the molar internal energy at this temperature and pressure is around –9.34 kJ mol^{-1}. It may help if you note that:

$$U = \frac{N_A}{2}\int_0^\infty N(r)u_{\text{pair}}(r)\text{d}r$$

(e) Sketch the form of the radial density function for the substance (i) at the same pressure but at higher temperatures, and (ii) at the critical point.

(d) Show that the contribution of the molecular interaction to the molar internal energy at this temperature and pressure is around –9.34 kJ mol^{-1}. It may help if you note that:

$$U = \frac{N_A}{2}\int_0^\infty N(r)u_{\text{pair}}(r)\text{d}r$$

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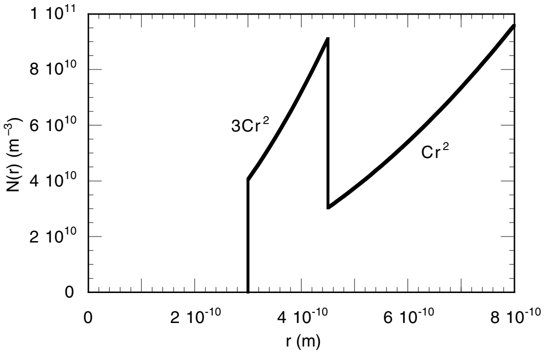


Solids

14. Young's modulus of simple solids

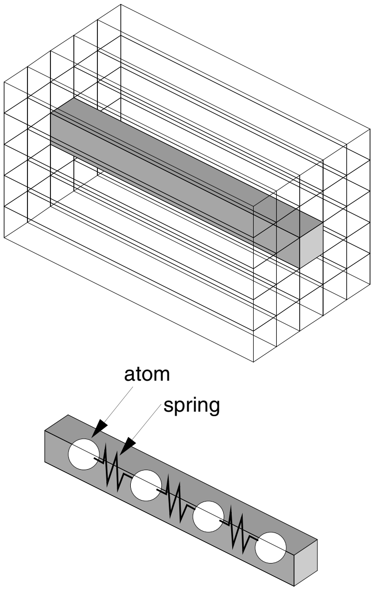
Many properties of solids can be understood on the basis of a simple model of a solid. The simplest version of the model assumes that each atom vibrates independently of its neighbours, like Figure 7.26(a) rather than Figure 7.26(b).

(a) The Einstein temperature of copper is 230 K and its density is 8933 kg m^{-3}. Based on the simple model above estimate values for (i) the Young's modulus, and (ii) the speed of longitudinal sound waves.

(b) Young's modulus E is defined by considering a long bar of unstressed length L under a tensile or compressive stress. In line with Equation 7.20:

$$\frac{\text{Force}}{\text{Area}} = E\frac{\Delta L}{L}$$

where [Force/Area] is known as the *tensile stress* and $\Delta L/L$ is the fractional extension of the bar and is know as the *tensile strain*. The 'trick' which allows us to do this is to think of the solid as being composed of essentially independent 'strings' of atoms. The key parameters you will need to estimate are K the 'spring constant' for the bonds between atoms; and a the interatomic spacing.



15. Schottky heat capacity anomaly

Consider a case where there are two quantum states on each atom in an elemental solid separated by $\Delta E = 2 \times 10^{-3}$ eV. This situation actually occurs at low temperature in some compounds where an ion is free to adopt two orientations. Normally there are more than two options, but the mathematics becomes even more complex and very little physics is added to the problem.

(a) Show that the probability of atom being in the upper and lower quantum states are given by:

$$P_{\text{lower}} = \frac{1}{1 + e^{-\Delta E / k_{\text{B}}T}}$$

$$P_{\text{upper}} = \frac{e^{-\Delta E / k_{\text{B}}T}}{1 + e^{-\Delta E / k_{\text{B}}T}}$$

Hint: The ion must be in one or other of these two orientations. So follow Example 2.8 and remember that $P_{\text{lower}} + P_{\text{upper}}$ must equal one.

(b) Show that the internal energy of 1 mole of the substance may be written as:

$$U(T) = U_{\text{o}} + N_{\text{A}} \left[\frac{\Delta E e^{-\Delta E / k_{\text{B}}T}}{1 + e^{-\Delta E / k_{\text{B}}T}} \right]$$

Make a graph of this function for temperatures from $T = 0$ K to $T = 3\Delta E/k_{\text{B}}$.

(c) Show that the constant volume heat capacity is:

$$C(T) = \frac{\Delta E^2 \times e^{\Delta E / k_{\text{B}}T}}{\left[e^{\Delta E / k_{\text{B}}T} + 1 \right]^2 k_{\text{B}} T^2}$$

Make a graph of this function for temperatures from $T = 0$ K to $T = 3\Delta E/k_{\text{B}}$. You should find that there is a large peak in the heat capacity (known as an *anomaly*).

(d) Numerically integrate $C(T)/T$ from $T = 0$ K to $T = 3\Delta E/k_{\text{B}}$ to show that the integrated entropy is close to $R\ln 2$.

The importance of this result is that from a measurement of the heat capacity of such a material, it is possible to identify the number of microscopic degrees of freedom available to the atoms. This relates to the entropy of the material (Example 10.2). The result holds in general and if the ions have p possible orientations the integral of $C(T)/T$ is $R\ln(p)$.

16. Asymmetry of pair potential: thermal expansion

In this question we will try to work out the coefficient of thermal expansion of a molecularly-bonded solid. Before starting I would just like to say that if you find this question straightforward you really should consider a career in physics. To do this we need to expand the Lennard-Jones 6-12 pair potential

$$u_{\text{pair}}(r) = -4\varepsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right] \qquad (1)$$

about its minimum.

(a) For simplicity let us consider only a single 'bond' between a pair of molecules. Differentiating $u_{\text{pair}}(r)$ we can find the value of r_{o} at the minimum. Show that $r_{\text{o}} = \left[2^{1/6} \right] \sigma$.

(b) Differentiate $u_{\text{pair}}(r)$ twice and evaluate the double differential at r_{o} to estimate the *curvature* of the potential. This is just the 'spring constant' of the bond, K. So if the curve were symmetric it would have the form:

$$u_{\text{pair}}(r) = u_{\text{pair}}(r_{\text{o}}) + K(r - r_{\text{o}})^2 \qquad (2)$$

Now equations such as Equation 1 are not as simple as quadratic equations and to solve this problem we need to take advantage of the fact that we know that near the bottom of the potential well the potential is *nearly* quadratic. Deviations from quadratic (harmonic) behaviour are small in comparison with the quadratic term. So we can first estimate the amplitude of vibration assuming that the curve is harmonic (Equation 2). This would lead to an oscillation symmetric about the equilibrium separation with the atom vibrating across Range 1 in the figure [labelled (a)] over the page. However, in the actual potential we see that the atom vibrates across Range 2 in the figure. Notice that Range 2 is not centred on the equilibrium separation but is shifted slightly to the right. The extent of this shift is what we wish to estimate.

(c) Estimate the amplitude of vibration A at temperature T assuming that the pair potential is quadratic.

(d) Figure (b) right shows how we can estimate Δx.

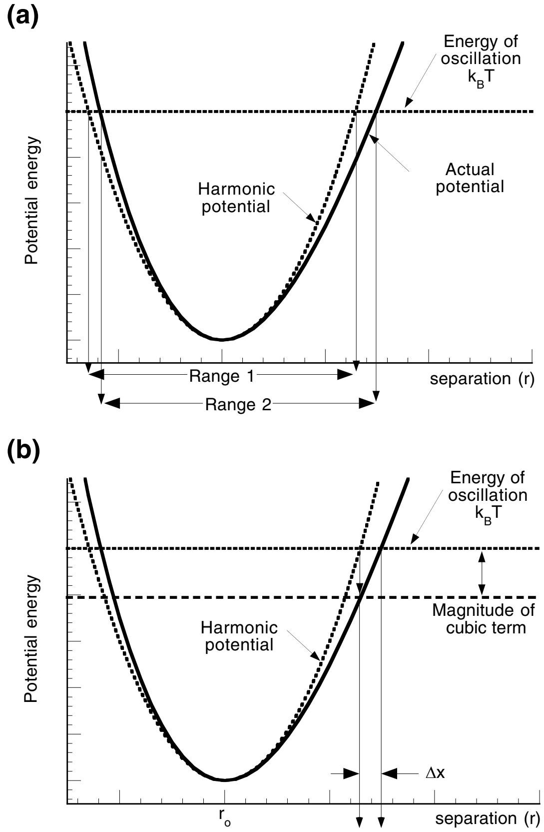
To do this we note that the slope of the actual potential close to the extrema of vibration at ($r_o \pm A$) is roughly:

$$\left.\frac{du_{\text{pair}}(r)}{dr}\right|_{(r_o \pm A)} \approx \frac{\text{deviation from quadratic at } (r \pm A)}{\Delta x}$$

Use this equation to evaluate Δx. To do this you will need to evaluate the *slope* of the actual potential at around $r_o \pm A$, and the difference between Equations 1 and 2 at these points. This yields the magnitude of the thermal expansion in a bond at temperature *T*. From this you can estimate the thermal expansion coefficient α, which is just the fractional bond expansion ($\Delta x/r_o$) per degree.

(e) Estimate the thermal expansion coefficient α for argon using the data from Table 6.2. Make sure you evaluate your estimate well below (say 50%) the melting temperature. The answer for argon is rather larger than for most solids: can you suggest a reason?

If you got this far: well done!



17. Force as derivative of potential

Consider a hypothetical element, the solid phase of which is composed of atoms interacting via a pair potential of the form:

$$u_{\text{pair}}(r) = A\left(e^{-2r/a} - 0.01e^{-r/a}\right)$$

This element forms a simple cubic solid with equilibrium separation between nearest neighbour atoms r_o. We will consider the properties of this element only at T = 0 K and neglect all interactions other than those between nearest neighbours.

(a) Make a graph of the function $u_{\text{pair}}(r)$.

(b) Show that the total molar cohesive energy is

$$U(r_o) = 3AN_A\left(e^{-2r_o/a} - 0.01e^{-r_o/a}\right)$$

and show that the equilibrium separation is $r_o = 5.3A$.

(c) What is the average cohesive energy per atom u_o in the crystal in equilibrium.

(d) The force between two atoms can be written:

$$F(r) = -\left(\frac{\mathrm{d}u_{\text{pair}}(r)}{\mathrm{d}r}\right)$$

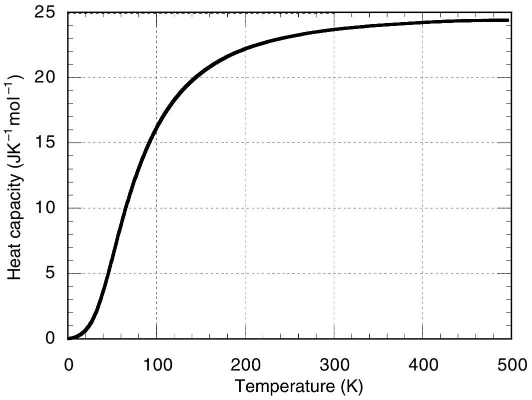
Make a graph of $F(r)$ for a pair of atoms. On your graph of $F(r)$ identify: (a) the point at which $u_{\text{pair}}(r) = 0$; (b) the point at which $\mathrm{d}u_{\text{pair}}(r)/\mathrm{d}r = 0$; (c) the point at which $u_{\text{pair}}(r)$ has a point of inflection.

(e) Assuming the simple solid model summarised in Figure 7.26 (a) and described in Question 14 is valid, estimate Young's modulus of this substance.

Note: It may help you to remember that:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(e^{bx}\right) = be^{bx}$$

18. Heat capacity



The graph shows the heat capacity of an elemental metal as a function of temperature. The density of the substance is 8.93×10^3 kg m^{-3} and the relative atomic mass is 64.

(a) Estimate the maximum energy of a phonon in this substance.

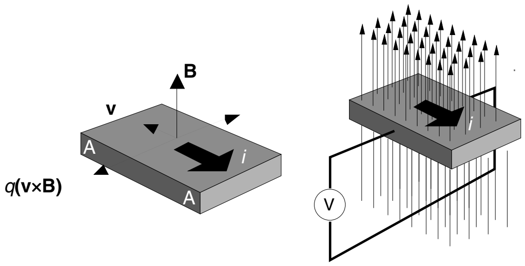
(b) Estimate roughly the speed of longitudinal and transverse sound waves in the substance.

(c) Estimate roughly the Young's modulus of the substance.

(d) Assuming the simple model of a solid summarised in Figure 7.26 and described in Question 14 is valid, estimate the 'spring constant' K for bonds between the atoms.

19. Hall effect

The Hall effect may be described as follows. When a magnetic field is applied perpendicular to a wafer of conducting material carrying a current along its length, then a potential difference appears across its width. This is illustrated schematically on the figure below.



The magnetic field **B** gives rise to a *transverse* potential difference V_H which we can understand by considering the following four points.

First: Consider the directions in which electrons move in the absence of an applied magnetic field. On the figure above I have drawn two arrows, representing the drift velocity **v** of an electron in the metal and the direction of conventional current flow.

Second: In an applied magnetic field **B**, each electron experiences an additional magnetic force $\mathbf{F}_m = q(\mathbf{v} \times \mathbf{B})$. Notice that because of the negative charge of the electron, $\mathbf{F}_m$ points in the opposite direction to the vector $(\mathbf{v} \times \mathbf{B})$.

Third: The magnetic force acts to 'push' electrons to the side of the sample marked A in the figure. Since the electrons cannot leave the sample by the side, the side A becomes negatively charged. The charging process builds up until an electric field created is sufficient to prevent any more electrons being pushed to side A. In other words, in the steady state – which is established a few picoseconds after the current begins to flow – the magnetic and electric forces are balanced and are of equal magnitude but opposite sign. In other words the Lorentz force is zero, which implies that $\mathbf{F}_e = -\mathbf{F}_m$. In this geometry, both $\mathbf{F}_e$ and $\mathbf{F}_m$ act along the x-axis and so their y- and z- components are both zero. Considering only the x-component of the vectors we can then write:

$$qE_H = qvB \qquad (1)$$

where E_H is the Hall electric field. Finally, in order to work out the potential difference V_H measured across the sample we need to recall two results:

- first, the electric field is just V_H/d where d is the width of the sample,
- second, the current can be written as $i = nAqv$, where n is the number density of charge carriers, A the cross-sectional area of the wire, q the charge on an individual carrier and v the average speed of the carriers.

(a) Using the information above show that the Hall voltage may be written as:

$$V_{\mathrm{H}} = \frac{i}{nqt}B \qquad (2)$$

where t is the thickness of the sample and q is the charge on an electron.

(b) Show that if the current were carried by positively charged carriers, the Hall voltage would have the opposite sign.

(c) For a gold film 1 μm thick a current of 1 mA produces a Hall voltage of 31.8 nanovolts in a perpendicular magnetic field of 0.3 T. Estimate the number density of electron carriers in gold.

(d) Semiconductors can have number densities of carriers n as low as (and sometimes much lower in fact!) than 10^{20} m^{-3}. For a sample 1 mm think estimate how many volts per tesla would be produced from the same measuring current if the semiconductor were used as a magnetic field detector. Would such a substance make a good magnetic field detector?

(e) Commonly the strength of the Hall effect for a substance is quantified in terms of a Hall constant R_{H},which is the Hall electric field per unit *current density* per unit magnetic field:

$$R_H = \frac{E_H}{jB} \qquad (3)$$

where j is the current density through the sample, i.e. the current per unit cross sectional area $j = i/td$ if the thickness is t and the width is d. Starting from Equation 3, show that the predicted value of R_{H} is:

$$R_H = \frac{1}{nq} \qquad (4)$$

My own experiments (during my PhD) on potassium metal yielded a value of $R_{\mathrm{H}} = -4.60 \times 10^{-10} \pm 0.14 \times 10^{-10}$ C^{-1} m^{3}. Is this the value that theory outlined in §6.5 would lead you to expect?

20. Intrinsic and extrinsic silicon

At absolute zero, a phosphorus impurity in silicon traps its 'extra' electron with a binding energy of $\Delta E_{\mathrm{d}} \approx 0.044$ eV.

(a) Estimate the temperature T_1 above which essentially all the phosphorus impurities are ionised and their electrons donated to the conduction.

(b) If the phosphorus concentration is 1×10^{19} m^{3} estimate the electron carrier density above T_1. What level of purity (in parts per million) does this correspond to? Would you describe such a material as 'pure'?

(c) The number density of electron carriers arising from the valence band n_{e} (as opposed to those arising from phosphorus impurities) is given *very roughly* by:

$$n_{\mathrm{e}} = n_{\mathrm{Si}} \exp\left[\frac{-\Delta E}{k_{\mathrm{B}}T}\right] \qquad (1)$$

where n_{Si} is the number of silicon atoms per cubic metre and ΔE is the energy gap in silicon (≈ 1.1 eV). At what temperature T_2 will the number density of electron carriers arising from the valence band equal the maximum number of donated electrons from the impurities. Above T_2 the silicon displays essentially the same properties as pure silicon and the impurities play only an insignificant part in conduction. Importantly, conduction is due to both electrons in the conduction band *and* an equal number of holes in the valence band. For silicon of this purity T_2 marks the temperature above which the sample behaves *intrinsically*. Below T_2 the conductivity of the silicon is dominated by the donated electrons from the phosphorus and this regime is known as the *extrinsic* regime. Between T_1 and T_2 the number of carriers is roughly constant.

(d) Estimate T_1 and T_2 for a sample with phosphorus impurities at a level of 10^{20} m^{-3}.

(e) Estimate the magnitude of the Hall constant (Question 19) from a sample of the above semiconductor (i) just above T_1 and (ii) just above T_2.

21. Mobility in metals and semiconductors

The resistivity of silver (the best conductor) at around room temperature is ≈ 1.59×10^{-8} Ω m and the resistivity of silicon with a concentration of 10^{22} phosphorus atoms m^{-3} is ≈ 5×10^{-3} Ω m.

(a) Calculate the scattering time τ and the mobility μ for electron carriers in each element.

(b) Surprisingly you will find that the mobility of electrons in silicon is much greater than in silver. Suggest a reason why this should be so. (Hint; the Debye temperature of silicon is 635 K and for silver it is 225 K.)

(c) Calculate the mobility for electrons in copper, silver, and gold. Does phonon scattering explain the trend in the mobilities of copper, silver, and gold? (See Table 7.12 for Debye Temperature and Table 7.13 for resistivity.)

(d) Calculate the drift velocity for electrons in silver and in silicon with a concentration of 10^{22} phosphorus atoms m^{-3} when a current of 1 mA is passed down wires of cross sectional area 10^{-6} m^2. (Hint: Equation 7.72b will help you to estimate the electric field.)

(e) For silver, compare the result in (d) with a calculation of the Fermi velocity of electrons. For silicon, compare this result in (d) with the mean speed of electrons calculated as if they were a Maxwell–Boltzmann type classical gas. (See §4.3). Comment on your results.

22. Light bulb design

An incandescent light bulb is essentially a heater: a small section of wire – the filament – is heated until its temperature is sufficient to cause it to glow. You might be surprised at how hot the filament becomes: in most light bulbs the temperature is around 1700 °C! Such extreme temperatures are required because the hotter the filament, the ‘whiter’ the light. However this requirement severely restricts the materials that can be used for a filament. Most commonly, the element tungsten is used. Let us try to work out how to design a filament for a 60 watt light bulb to operate from a 220 V supply. This is the kind of light bulb you might be using in a desk lamp as you read this. It might not seem to be much of challenge to ‘design a piece of wire’ but as you will see, working out the length L and diameter d of the wire is more complicated than it seems.

The key to designing a light bulb is to realise that it is essentially an energy transducer, i.e. it changes electrical energy to radiant energy in the form of electromagnetic waves. Thus we want to put in 60 watts of electrical energy and get out 60 watts of radiant energy.

(a) Assuming that the electrical resistivity of tungsten at around 2000 K is $\approx 5 \times 10^{-7}$ Ω m, work out the ratio of the length to the cross-sectional area of the wire L/d of a piece of wire that will dissipate $P = 60$ W.

The rate at which radiant energy leaves a surface of area S at absolute temperature T is given by Stefan’s law: $P = \sigma S T^4$ where σ is the Stephan-Boltzmann constant $\sigma = 5.57 \times 10^{-8}$ W m^{-2} K^{-4}. In fact this Equation applies exactly only to the surface of a hypothetical material known as a ‘black body’. However, it can be used as a rough approximation for most real substances. (See part (d) for how to go beyond this approximation.)

(b) Show that the energy radiated from a wire in terms of its length and diameter d:

$$P = \left(\pi \sigma T^4\right) dL$$

(c) In order to make our light bulb work, we need to choose values for L and d which causes both 60 W energy electrical dissipation (part (a)) and 60 W of radiated energy to be radiated (part (b)). Hence derive separate expressions for d and L. Assuming that the light bulb will operate at around 2000 K, estimate the length and diameter of the filament.

(d) Break open a light bulb (carefully!) and check your calculation. You will probably find that you got the diameter of the wire about right, but overestimated the length of the wire. What factors do you think could account for this difference? One of the factors is the *emissivity* ε of tungsten, which describes the deviation of the emission of the surface from the black body condition. Thus the actual amount of energy radiated is given by $P = \varepsilon \sigma S T^4$. Can you estimate a value of ε for tungsten from your measurements?

(e) Finally, note that I have considered only conventional light bulbs. Tungsten halogen bulbs run much hotter than normal light bulbs, and this calculation will very severely overestimate the length of filament required for such bulbs. You can recognise such bulbs because they are (a) much smaller than normal bulbs and (b) much brighter, giving a whiter (or in fact bluer) light than normal light bulbs.

23. Low temperature heat capacity

T (K)	Molar heat capacity (mJ mol^{-1} K^{-1})
1.0	0.84
1.5	1.53
2.0	2.72
2.5	4.2
3.0	6.42
3.5	9.24
4.0	13.2

The table above shows data on the low temperature heat capacity C of a substance.

(a) Plot this data on a graph as C/T versus T^2. How can you tell this element is a metal?

(b) Estimate the density of states at the Fermi energy.

(c) Assuming that the density of states has the free electron form (See Equation 6.70 and Example 7.14) estimate the Fermi energy in electron volts.

(d) The Debye theory of the phonon heat capacity of a solid (Appendix A4) predicts that when $T \ll \Theta_D$:

$$C(T) = 9R\left(\frac{T}{\theta_D}\right)^3 \quad [25.976]$$

Use this equation and the data above to estimate the Debye temperature of the sample.

(e) Estimate the speed of sound in the sample.

(f) Estimate the heat capacity of the element at a temperature of 500 K.

24. Packing fractions

When thinking about crystal structures in solids it is often helpful to think of atoms as hard spheres. On this assumption, work out the fraction of space (known as the *packing fraction*) that is occupied by spheres when they are packed in

(a) simple cubic,

(b) body-centred cubic, and

(c) face-centred cubic structures.

Note that in the simple cubic structure, the spheres on adjacent corners just touch (or as it is known technically: *kiss*). In a body-centred cubic structure, the eight spheres at the corners of the cube do not touch each other but they all kiss the central sphere. And in a face-centred cubic structure the sphere at the centre of each face kisses the four spheres at the corners of that face. You should find that face-centred cubic structure yields the most efficient packing, but you may be interested to know that it is currently not mathematically possible to *prove* that this is the case!

25. Solid helium

At low temperatures and atmospheric pressure, helium – uniquely – does not solidify. Under pressure, helium can be solidified, and as the pressure is increased, it goes through a succession of ever denser crystal structures. Under a pressure of 37 atmospheres at 1.7 K, helium has a body centred cubic (*bcc*) structure with a density of 200 kg m^{-3}. In this question we will try to understand why the crystal structure adopted is *bcc* (Figure 6.6 (a)) and not *fcc* (Figure in Example 6.1) as adopted by the other noble gases.

(a) Estimate the side of the *bcc* conventional unit cell and the nearest neighbour separation.

(b) The parameters of the Lennard–Jones pair potential estimated from the gas phase are $\sigma = 2.56 \times 10^{-10}$ m. and $\varepsilon = 1.406 \times 10^{-22}$ J. Using the values of the lattice sums for *bcc* from Table 6.1, estimate the nearest neighbour separation you would expect to find and compare it with the answer in (a).

You should find that the answer to part (b) is considerably smaller than the experimental near neighbour separation determined in (a). So the phenomena we need to understand are (i) why helium first solidifies in a *bcc* structure and (ii) why the nearest-neighbour separation is greater than would be estimated on the basis of the Lennard–Jones potential.

The factor we have not considered is that the atoms are intrinsically quantum mechanical objects. When confined to a small volume there is a minimum energy – the so-called *zero point energy* – that the particle must have. Let us try to model this by adding the energy of a particle in a box of side L (Equation 2.49) to Equation 6.18. We estimate that the energy per atom is:

$$\frac{U}{N_A} = 2\varepsilon A_{12}\left(\frac{\sigma}{r_o}\right)^{12} - 2\varepsilon A_6\left(\frac{\sigma}{r_o}\right)^6 + \frac{3h^2}{8m_{He}L^2} \qquad (1)$$

where the last term is the lowest energy of a helium atom in a three-dimensional cubic box of side L. Of course, each helium atom is not confined to a cubic box of this (or any other) size, but is constrained by a complicated potential. In this question we will estimate roughly that $L \approx 0.7r_o$.

(a) Evaluate the coefficient of r_o or L in each term in Equation 1 and plot each term in Equation 1 as a function of r_o on the same graph.

(b) Plot (i) the sum of the first two terms and (ii) the sum of the first three terms in Equation 1 as a function of r_o (roughly from around σ to 1.2σ). You should see that the minimum of the curve has been moved to a larger value of r_o and reduced in its depth by a considerable amount. You will not be able to get the actual value of the new lattice constant right, but you should see that the new curve has a minimum which is only just below the zero of energy, i.e. the binding is very weak.

(c) Evaluate the last term in Equation 1 – the quantum mechanical term – for neon, argon and krypton, and compare your results with the cohesive energy of these substances in Table 6.2. You should find that the quantum mechanical correction is small for substances other than helium and (to a much smaller extent) neon.

(d) The packing fraction for *bcc* is less than for *fcc*. Taking this into account, explain briefly why helium solidifies first in the *bcc* structure.

Optional. If you wish to understand solid helium more fully, consider Equation 1 evaluated with lattice sums appropriate to the *fcc* structure. Compare these results with the evaluation you made for the *bcc* structure. For *fcc* you will have to choose a value for L which will be a smaller fraction of r_o than the factor 0.7 chosen for *bcc*. This is because the more efficient packing of atoms in a *fcc* structure more tightly constrains the helium atoms.

26. Beyond Einstein!

The Einstein model of vibrations in solids assumes that all atoms are identical and all vibrate with a single frequency. The Debye model is more realistic, allowing for a spectrum of allowed vibrational frequencies. However, in between the two models there were historically a plethora of modifications of the Einstein model, which assumed 'a few' vibrational frequencies.

(a) Assuming that 50% of the atoms vibrate with frequency f_1 and 50% with frequency f_2, work through the equations in Appendix A4 (or Equations 7.48 to 7.56) and show in a similar fashion that the heat capacity predicted by such a model is given by:

$$C = \frac{3R}{2T^2}\left[\frac{\Theta_1^2\exp(\Theta_1/T)}{\left(\exp(\Theta_1/T)-1\right)^2} + \frac{\Theta_2^2\exp(\Theta_2/T)}{\left(\exp(\Theta_2/T)-1\right)^2}\right]$$

where $\Theta_1 = hf_1/k_B$ and $\Theta_2 = hf_2/k_B$.

(b) Show that this has the same high-temperature limiting value (law of Dulong and Petit) as the Einstein expression (Equation 7.56).

(c) Sketch - either qualitatively or by direct use of a spreadsheet - the general shape of this new curve when $f_1 = 10f_2$.

(d) Suggest (with some attempt at justification please) what kind of substances such a model might have been developed to describe.

27. Low-temperature resistivity of metals

The graph over the page shows the electrical resistivity of a sample of copper which contains small amounts of zinc impurity. The units of ρ on the vertical scale are 10^{-8} Ωm. At absolute zero, lattice vibrations are unable to scatter electrons. The scattering which gives rise to the so-called *residual resistivity* is due solely to impurities and defects in the crystal lattice.

A general rule, called *Mattheison's rule*, states that the resistivity arising from different sources may be simply added to give the total resistivity:

$$\rho_{total} = \rho_{impurity} + \rho_{phonons} \qquad (1)$$

Assuming Mattheison's rule to hold:

(a) At 0 K, work out the resistivity due to impurities and that due to phonons.

(b) At 300 K, work out the resistivity due to impurities and that due to phonons.

(c) It is known that zinc impurities in copper add to the resistivity an amount:

$$\rho_{\text{zinc/copper}} = 4\times10^{-9}\, c_{\text{zinc/copper}} \quad \Omega\,\text{m}$$

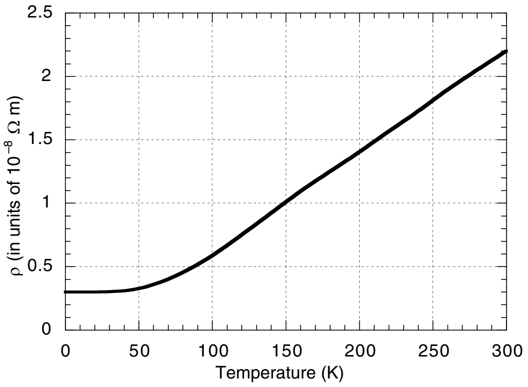
where $c_{\text{zinc/copper}}$ is the concentration of zinc in copper in atomic percent. (See discussion in §7.4 of an $A_X B_{1-X}$ alloy: the alloy has x atomic percent of element A.) Assuming no other significant amounts of impurity are present, what is the concentration of zinc in this particular sample?

(d) Make a sketch of the curve of $\rho(T)$ that you would expect if the concentration were twice as great as that found in (c).

(e) Estimate the time between scattering events at $T = 0$ K.

(f) Copper has a number density of electrons of around $8.65 \times 10^{28}\ \text{m}^{-3}$. Estimate the speed of electrons at the Fermi surface and hence estimate the mean free path between scattering events. Compare your answer with the expected distance between impurities inferred from your answer to (c). Do they agree?

(g) The measurements shown were deduced from measurements on a sample 3 cm long and 1 mm in diameter. If the measuring current was 50 mA, estimate the voltage measured experimentally. The resistivity of superconductors is known to be $<10^{-25}\ \Omega$ m. Based on your answer to this question explain why data on the resistivity of superconductors has to be inferred from measurements other than direct measurements of resistivity.



Changes of Phase

28. Water phase diagram

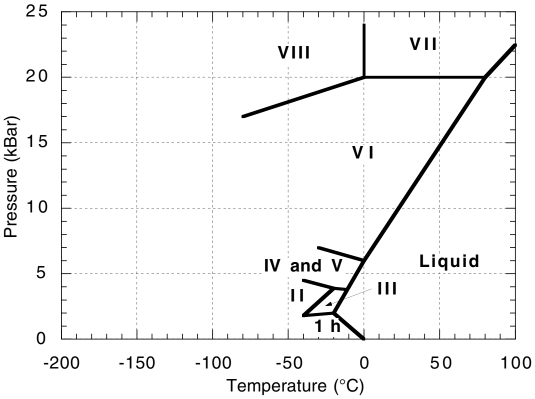


Figure 10.16 shows a phase diagram for water substance constructed on the basis of extrapolation of the theoretical expressions for the melting and vaporisation curves. These expressions do not remain accurate at very high pressures because the normal ice structure, called Ice I (or Ice Ih where the h stands for *hexagonal*), collapses into a series of ever-denser structures. The experimentally determined phase diagram of ice is shown above. The roman numerals indicate regimes of temperature and pressure in which ice adopts one its ten different crystal structures. The *full* phase diagram is even more complicated than the one shown and includes a large number of metastable crystal structures.

(a) The vertical scale on the pressure axis is in kilobar, where one bar is normal atmospheric pressure. On the diagram above sketch the area to which Figure 10.16 applies.

(b) What is the minimum melting temperature for ice, and at what pressure does it occur?

(c) Over roughly what temperature range would applying pressure to ice first cause the ice to melt, and then at higher pressures to solidify?

(d) What pressure would be required to solidify water at room temperature?

(e) At what pressure would water freeze at 100 °C? Is it feasible to ever measure this?

(f) Which solid structures have a volume less than that of the liquid at that pressure?

(g) Let us just suppose there is some water deep within the Earth near to the core–mantle boundary. The pressure at this depth is around 10^{11} Pa. Extrapolating (wildly!) from the phase diagram, estimate the freezing temperature of water in this region. If the water were solidified, what structure would it adopt?

29. Corresponding states

The atoms of a hypothetical element *Podestium* have mass 10^{-25} kg and in their solid state adopt a simple cubic structure with nearest neighbours separated by 4×10^{-10} m. They undergo three-dimensional simple harmonic motion about fixed equilibrium positions with a period of 5×10^{-13} s.

(a) Estimate the melting temperature of the solid. What uncertainty would you ascribe to your estimate?

(b) Based on your answer to (a), estimate the boiling temperature of the liquid. What uncertainty would you ascribe to your estimate?

(c) Estimate the critical temperature of the substance.

(d) Estimate the critical volume of the substance.

30. *PVT* journey.

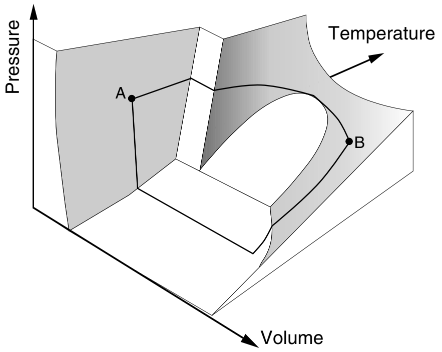
The figures on the right show two generic *PVT* surfaces. The drawings are poor, but in the upper figure, points *A* and *B* are intended to describe points at the same pressure, and in the lower figure, points *C* and *D* are intended to describe points at the same volume.

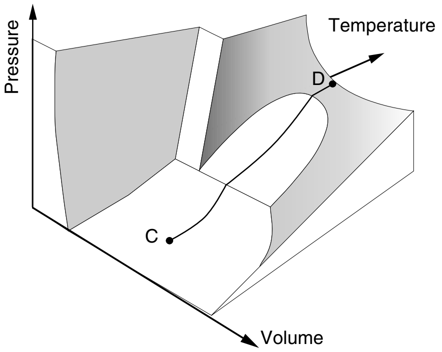
(a) A substance is taken on a 'journey' across the *PVT* surface shown from point *A* to point *B* and then back to point *A* by a different 'route'.

(b) A substance is taken on a 'journey' across the *PVT* surface shown from point *C* to point *D*.

Describe each journey (a) and (b) in as much detail as possible, including descriptions of:

- The phase (or phases) of the substance present at each stage on its journey. Where relevant discuss the relative amounts of the phases present.
- The rates of changes of *P*, *V* and *T*.
- The points along the paths where heat enters or leaves the substance;
- The points along the paths where work is done by or on the substance;
- Anything else relevant!





Shorter Questions

1. Exploding tube

A cylindrical tube has one closed end and one open end? 10^{-4} m^3 of helium at room temperature and pressure is sealed in the tube by a stopper. The stopper is then glued into place so as to make it gas-tight. The tube is then heated and at 500 K the glue melts and the stopper pops out of the tube *suddenly*. Estimate the volume and temperature of the helium gas just after it leaves the tube.

2. γ Factor.

Calculate the ratio of initial to final volumes in an adiabatic compression capable of heating air from 293 °C to 500 °C. If you do this experiment and put a few pieces of dry paper in the container they will catch fire: be careful!

3. The Chromosphere of the Sun

In the chromosphere of the sun — the outer part which radiates light directly to us — the temperature is $\approx 10^4$ K and the pressure is $\approx 10^{-8}$ Pa. At these temperatures Hydrogen molecules are broken apart into atomic Hydrogen. Estimate the speed and mean free path for Hydrogen atoms in this region.

4. Ultra High Vacuum

In many modern processes it is essential that contamination of a surface by atoms from the gas phase is kept to an absolute minimum. To achieve this such processes are carried out under what is known as Ultra High Vacuum (UHV) conditions. Using specialised equipment, and with great care, pressures of around 10^{-8} Pa are possible. If a gas above a surface is at such a pressure, work out the average number of collisions per hour of gas molecules with a particular atom in the surface.

5. Compressibility of Copper.

A copper cube of volume 1 cm^3 is held at room temperature while an external pressure on it is increased from 1 atmosphere to 10^8 Pa (approximately 1 kbar). If the isothermal compressibility of copper is:

$$K_{\text{iso}} = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_{\text{T Constant}} = 7.4\times10^{-12}\ \text{Pa}^{-1},$$

estimate the change in the volume of the cube and (using a simple model of a solid) the percentage change interatomic separation.

6. Relative probabilities.

An atom in a solid has two possible quantum states separated in energy by ΔE. The lower state has a probability of being occupied of 0.9.

(a) Calculate the temperature in terms of ΔE.

(b) If the chance of both the upper and lower states being occupied is 0.5, what is the temperature?

(c) Is it possible for the probability of occupying the upper state to ever exceed the probability of occupying the lower state?

7. Ionic Solid.

The Madelung constant for an ionic solid with the NaCl structure is 1.748 and the repulsive term between nearest neighbours has the form c/r^{12} where $c = 4.86\times10^{-134}$ J m^{12} (or $c = 4.86\times10^{-23}$ J$(\text{nm})^{12}$). Calculate the nearest neighbour separation and the cohesive energy per ion.

8. Molecular Solid.

The Lennard-Jones potential between atoms can be written as:

$$\varepsilon(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

Calculate the ratio B/A if the equilibrium separation is 5×10^{-10} m.