

Chapter 6 Answers

These are answers to the questions in Chapter 6 of:

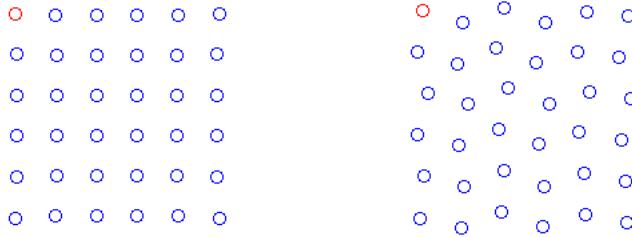
Understanding the Properties of Matter
by Michael de Podesta.

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

C1. The initial ‘square’ structure and the hexagonal structure into which ‘collapses’ into a ‘hexagonal’ structure are shown below.



Can I explain why this happens? Mmmm. At zero temperature, the hexagonal structure definitely has a greater cohesive energy. This is so because the interactions in this model are 2-D Lennard–Jones type interactions. Just as in the three dimensional case, the cohesive energy is maximised by maximising the number of nearest neighbours and in two dimensions this is achieved by the hexagonal structure you observe.

However, the temperature in this model is not zero, and indeed the simulation conserves energy (at least it should, but it doesn’t quite!). What has happened is that energy has been swapped from being nearly entirely potential energy in the square lattice, to being a mixture of kinetic and potential energy in the hexagonal case. In physical terms we have a sample of material with the square structure at a very low temperature which then spontaneously transforms to the hexagonal structure with the release of some latent heat (enthalpy of transformation). In Chapter 10 we state that the reasons that such a change takes place is because the second structure minimises what is called the *Gibbs free energy*.

C2. I’m afraid you just have to do this one for yourself. The only point I think worth making is that the position and depth of the minima depend on ratios of A and B raised to their respective powers as expressed in Equation 6.8

$$\sigma = \left[\frac{B}{A} \right]^{1/6} \quad \text{and} \quad \epsilon = \left[\frac{A^2}{4B} \right] \quad (6.8)$$

P3. $\sigma = 0.365 \text{ nm}$ and $\epsilon = 0.014 \text{ eV}$

(a) Molar cohesive energy is predicted to be just N_A times the value per atom which amounts to

$$-8.6\epsilon N_A = 11.602 \text{ kJ mol}^{-1}$$

This can be compared with the value of 11.2 kJ mol^{-1} in Table 11.5.

(b) The equilibrium separation of atoms r_0 is predicted to be 0.398 nm . The problem now is to relate the volume of a face-centred cubic unit cell to r_0 . To do this we note that the diagonal across a face of the cell has length $2r_0$. So using Pythagorus’ theorem we may write

$$\begin{aligned}
 a^2 + a^2 &= (2r_0)^2 \\
 a^2 &= \frac{4r_0^2}{2} = 2r_0^2 \\
 a &= \sqrt{2}r_0
 \end{aligned}$$

The volume of such a cube will therefore be

$$V = a^3 = 2\sqrt{2}r_0^3$$

Such a cub wholly contains 8 eighths of atoms at its vertices, and 6 halves of atoms at the centres of its faces making a total of 4 atoms, each with mass $M_{\text{Kr}} = 83.8 \times 1.66 \times 10^{-27} \text{ kg}$ and so its predicted density is

$$\begin{aligned}
 \rho &= \frac{4M_{\text{Kr}}}{V} = \frac{4M_{\text{Kr}}}{a^3} = \frac{4M_{\text{Kr}}}{2\sqrt{2}r_0^3} \\
 &= \frac{\sqrt{2}M_{\text{Kr}}}{r_0^3} \\
 &= \frac{\sqrt{2} \times 83.8 \times 1.66 \times 10^{-27}}{(0.398 \times 10^{-9})^3} \\
 &= \frac{1.967 \times 10^{-25}}{6.304 \times 10^{-29}} \\
 &= 3121 \text{ kg m}^{-3}
 \end{aligned}$$

From Table 7.2 the experimental answer is 3000 kg m^{-3} .

C4. I do not have an answer available for this question.

P5. In §6.3 we considered calculations of the potential energy of electrons in a covalent bond, but did not consider their kinetic energy. The kinetic energy is difficult to calculate accurately, but one can estimate it roughly by considering the electrons in the bond region of length L to be confined to . The kinetic energy of an electron in a three dimensional box of side L is:

$$KE = \frac{h^2}{8m_e L^2} [n_x^2 + n_y^2 + n_z^2]$$

For the ground state the energy is

$$\begin{aligned}
 KE &= \frac{h^2}{8m_e L^2} [1^2 + 1^2 + 1^2] \\
 &= \frac{3h^2}{8m_e L^2}
 \end{aligned}$$

For the C–C bond we considered in Chapter 6 the bond length is $r_0 \approx 0.13 \text{ nm}$ so assuming $L \approx r_0$ we find

$$\begin{aligned}
 KE &\approx \frac{3 \times (6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} (0.13 \times 10^{-9})^2} \\
 &\approx 1.069 \times 10^{-17} \text{ J} \\
 &\approx 66 \text{ eV}
 \end{aligned}$$

As I stated in the question this is very large energy and the certainly an overestimate of the electron energy. It is an overestimate because the electron is not really confined to this small region but is able to 'leak' into the region around each atom.

P6. Following example 7.3 we find that the density of silicon or germanium may be written as

$$\text{density} = \frac{\text{mass of atoms in unit cell}}{\text{volume of unit cell}}$$

For the unit cell in question there are 4 atoms wholly in the unit cell, 8 atoms at the vertices of the unit cell which are each shared between 8 other unit cells, 6 atoms in the centre of the faces each of which is shared between 2 unit cells.

$$\begin{aligned}
 \text{density} &= \frac{[4 \times 1 + 8 \times \frac{1}{8} + 6 \times \frac{1}{2}] \times \text{mass of atom}}{\text{volume of unit cell}} \\
 &= \frac{[8] \times \text{mass of atom}}{\text{volume of unit cell}}
 \end{aligned}$$

We then need to work out a relationship between the nearest neighbour separation r_0 and the side of the unit cell L . The trick required to achieve this is to notice that the bond length is just a quarter of the length of the *body diagonal* of the unit cell. (The body diagonal is the line from one vertex of a cube to the opposite vertex running through the centre of the cube.) The body diagonal is related to the side of the unit cell L by:

$$\begin{aligned}
 \text{body diagonal} &= \sqrt{L^2 + L^2 + L^2} \\
 &= \sqrt{3}L
 \end{aligned}$$

and so we find:

$$\begin{aligned}
 \text{body diagonal} &= 4r_0 = \sqrt{3}L \\
 L &= \frac{4r_0}{\sqrt{3}}
 \end{aligned}$$

and so we can write the density as

$$\begin{aligned}
 \text{density} &= \frac{[8] \times \text{mass of atom}}{L^3} \\
 &= \frac{[8] \times \text{mass of atom}}{\left[\frac{4r_0}{\sqrt{3}} \right]^3} \\
 &= \frac{8\sqrt{3}^3 \text{ mass of atom}}{64 r_0^3} \\
 &= \frac{3\sqrt{3} \text{ mass of atom}}{8 r_0^3}
 \end{aligned}$$

And so we can invert this to predict that:

$$r_0 = \left[\frac{3\sqrt{3} \text{ mass of atom}}{8 \text{ density}} \right]^{1/3}$$

(a) For silicon we find

$$\begin{aligned}
 r_0 &= \left[\frac{3\sqrt{3} \cdot 28.09 \times 1.66 \times 10^{-27}}{8 \cdot 2329} \right]^{1/3} \\
 &= 2.35 \times 10^{-10} \text{ m} \\
 &= 0.235 \text{ nm}
 \end{aligned}$$

(b) For germanium we find

$$\begin{aligned}
 r_0 &= \left[\frac{3\sqrt{3} \cdot 72.59 \times 1.66 \times 10^{-27}}{8 \cdot 5323} \right]^{1/3} \\
 &= 2.45 \times 10^{-10} \text{ m} \\
 &= 0.245 \text{ nm}
 \end{aligned}$$

These answers are curiously similar which bears out our general assertion that bond lengths don't systematically increase with atomic number.

P7. You should get answers something like the following table which is an extension of Table 6.3:

nx	ny	nz	Energy	Degeneracy	inc spin	Running total of the number of electrons that can accommodated	2	3	4	<<<size of the side of the box in units of a <<<number of electrons to accommodate	
1	1	1	3	1	2	2	6	6	6		
1	1	2	6	3	6	8	36	36	36	<<<2 x 2 x 2 box maxi- mum occupied energy	
1	2	2	9	3	6	14		54	54		
1	1	3	11	3	6	20		66	66		
2	2	2	12	1	2	22		24	24		
1	2	3	14	6	12	34		70	168	<<<3 x 3 x 3 box maxi- mum occupied energy	
2	2	3	17	3	6	40			102		
1	1	4	18	3	6	46			108		
1	3	3	19	3	6	52			114		
1	2	4	21	6	12	64			252	<<<4 x 4 x 4 box maxi- mum occupied energy	
2	3	3	22	3	6	70					
3	3	3	27	1	2	72					
1	1	5	27	3	6	76					
							42	256	354	<<<total n ² factors	
							10.50	28.44	22.13	<<< dividing through by the enlarged box sizes = total energy	
							Option B answer>>>>	1.31	1.05	0.35	
										<<< dividing through by the number of electrons to find the average energy per electron in units of h ² /8ma ²	
							Option A answer>>>>	3	3	3	
										energy difference between option A and B per electron>>>>	
								1.69	1.95	2.65	
								energy difference between option A and B per electron for large boxes>>>>	2.42	2.42	2.42
										<<< limiting answer for large boxes (Equation 6.87)	

The limiting value for large boxes (i.e. the free electron gas value) is obtained from Equation 6.87 by taking the factor 3 from the numerator and multiplying the prefactor (-0.806). Bone fide educators may e-mail me for a copy of the spreadsheet on which this table is based. However to develop the calculation beyond the 4 x 4 x 4 box I would strongly recommend using custom software (written in BASIC or FORTRAN or C etc.) rather than using a spreadsheet.

C8. When the simulation is running turn off the radio button for molecular interactions and observe the destruction of the solid. This should not be difficult to observe.

Would the solid state be possible without molecular interactions? No.