

BSc/MSci EXAMINATION

PHY-108 Condensed Matter

Time Allowed: 2 hours 15 minutes

Date:

Time:

Answer ALL questions in section A. Answer ONLY TWO questions from section B. Section A carries 40 marks, each question in section B carries 30 marks. An indicative marking-scheme is shown in square brackets [] after each part of a question.

COMPLETE ALL ROUGH WORKINGS IN THE ANSWER BOOK AND CROSS THROUGH ANY WORK WHICH IS NOT TO BE ASSESSED.

NUMERIC CALCULATORS ARE PERMITTED IN THIS EXAMINATION.

Data

Electronic charge	$e = -1.60 \times 10^{-19}$	C
Mass of electron	$m_e = 9.11 \times 10^{-31}$	kg
Avogadro constant	$N_A = 6.02 \times 10^{23}$	mol ⁻¹
Universal gas constant	$R = 8.31$	J mol ⁻¹ K ⁻¹
Boltzmann's constant	$k_B = 1.38 \times 10^{-23}$	JK ⁻¹
Atomic mass unit	$1 \text{ amu} = 1.66 \times 10^{-27}$	kg

YOU ARE NOT PERMITTED TO START READING THIS QUESTION PAPER UNTIL INSTRUCTED TO DO SO BY AN INVIGILATOR

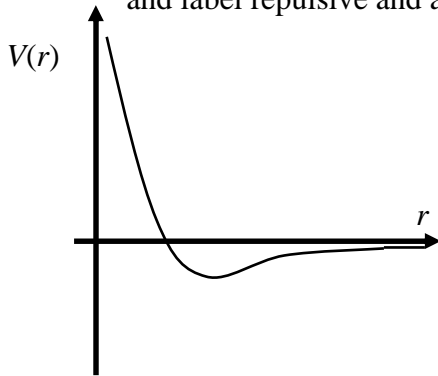
Examiners: Dr. A. Sapelkin, Dr. T. J. S. Dennis

Section A

A1. What is the mathematical relationship between the force and the potential? [3]

Ans: $F(r) = -dV/dr$

A2. Sketch the potential energy versus distance diagram for a pair of electrically neutral atoms. Write down corresponding expression for Lenard-Jones potential and label repulsive and attractive terms. [5]



$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

A3. What is the physical significance of the minimum potential energy? [3]

Ans: it corresponds to binding energy

A4. What is the nature of van der Waals force? Is there a similarity between the origins of ionic and van der Waals interaction? [4]

Ans: Van der Waals bonding arises from the polarization of molecules into dipoles. Ionic bonding is due to electrostatic interaction of positively and negatively charged ions. Both are due to electrostatic attraction.

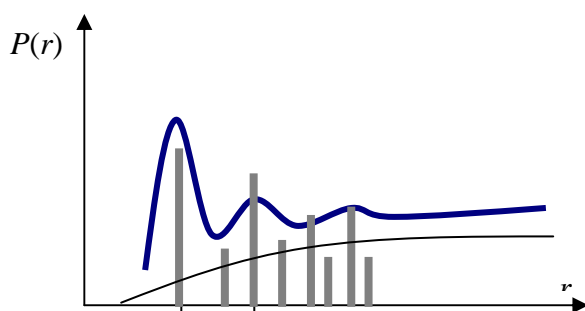
A5. What macroscopic property defines the size of a droplet in gravitational field of the Earth? [4]

Ans: Surface tension

A6. Give the definition of bulk modulus k and of compressibility. [4]

Ans: $k = -VdP/dV$, compressibility is $1/k$

A7. Sketch radial distribution functions $P(r)$ for a solid, liquid and gas. [3]



A8. Give the definition of pressure. [2]

Ans: $P=F/S$

A9. What is a phonon? [3]

Ans: mode of lattice vibration

A10. What are the main features of Einstein and Debye models of specific heat? [5]

Ans: The former is an independent oscillator approximation, while the latter is a continuous medium approximation

A11. Which has a wider band gap (the gap between valence and conduction band): an insulator or a semiconductor? How metals are different in this respect? [4]

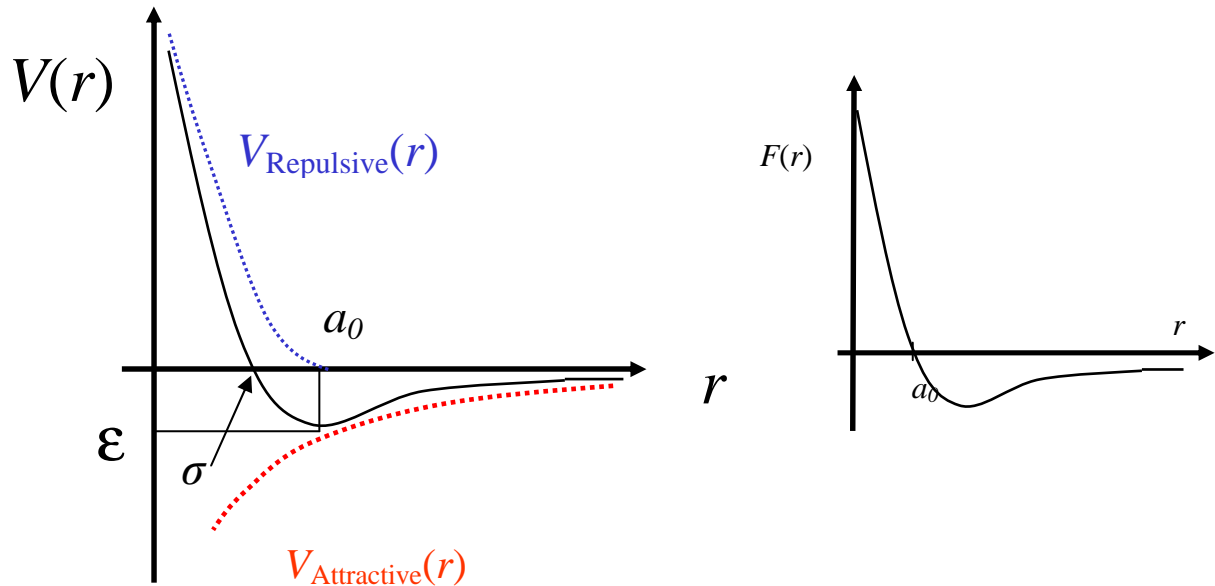
Ans: insulator has a wider band gap. Metals have zero band gap

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Section B

B1. (i) . (i) Sketch the interatomic potential corresponding to the van der Waals interaction and mark the repulsive term, attractive term, dissociation energy, equilibrium separation, and atomic diameter. Sketch corresponding diagram for the force and mark equilibrium separation.

[9]



(ii) Interatomic potential is given by

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right].$$

Use equilibrium separation value $a_0 = 0.2$ nm and dissociation energy value (energy necessary to break the molecule) $E_{\text{diss}} = 2 \times 10^{-18}$ J.

- (a) Calculate σ . [3]
 (b) Find the force necessary to reduce a_0 by 1%. [5]
 (c) Find the force necessary to break the molecule. [6]

Ans:

a. $\left. \frac{dV}{dr} \right|_{a_0} = 0 \Rightarrow \sigma = 2^{\frac{1}{6}} a_0 \approx 0.89 * a_0 \approx 0.18 \text{ nm}$

b.
$$F(0.99a_0) = - \left. \frac{dV(r)}{dr} \right|_{0.99a_0} = 4\epsilon \left(-12 \frac{\sigma^{12}}{r^{13}} + 6 \frac{\sigma^6}{r^7} \right) \Bigg|_{0.99a_0} = 4\epsilon \left(-12 \frac{(0.89a_0)^{12}}{(0.99a_0)^{13}} + 6 \frac{(0.89a_0)^6}{(0.99a_0)^7} \right) \approx$$

$$4\epsilon * \left(- \frac{12 * 0.28}{a_0} + \frac{6 * 0.5}{a_0} \right) = -4\epsilon * 0.2 / a_0 = -8 * (-10^{-18} \text{ J}) / a_0 = 8 * 10^{-9} \text{ J/m} = 8 * 10^{-9} \text{ N}$$

c. Max force will be required to break molecule. Hence, need to find critical distance r_c , at which $dF(r)/dr = 0$. Then substitute that distance into expression for force.

$$\frac{dF(r)}{dr} = 156 \frac{\sigma^{12}}{r_c^{14}} - 42 \frac{\sigma^6}{r_c^8} = 0, r_c = \left(\frac{156}{42} \right)^{1/6} \sigma \approx 1.25\sigma \approx 0.22 \text{ nm}$$

$$F(r_c) = 4\epsilon \left(-12 \frac{\sigma^{12}}{r_c^{13}} + 6 \frac{\sigma^6}{r_c^7} \right) \approx 4 * 2 * 10^{-18} * \left(-12 \frac{\sigma^{12}}{1.25^{13} * \sigma^{13}} + 6 \frac{\sigma^6}{1.25^7 * \sigma^7} \right) \approx$$

$$8 * 10^{-18} * (-3.7 + 6.3) * 10^9 \text{ N} = 20.8 * 10^{-9} \text{ N}$$

(iii) For $V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^p - \left(\frac{\sigma}{r} \right)^q \right]$,

show that if $p \gg q$, then total energy will be defined by attraction energy. Show that a minimum of $V(r)$ is only possible if $p > q$ (hint: use condition $d^2V/dr^2 > 0$). [7]

Ans:

$$\frac{dV}{dr} = 0; \frac{d^2V}{dr^2} > 0; p \frac{\sigma^p}{r^{p+1}} = q \frac{\sigma^q}{r^{q+1}}$$

$$p(p+1) \frac{\sigma^p}{r^{p+2}} - q(q+1) \frac{\sigma^q}{r^{q+2}} > 0 \Rightarrow (p+1) \frac{1}{r} > (q+1) \frac{1}{r} \Rightarrow p > q$$

B2. (i) Using the definition of surface tension via binding energy and surface number density evaluate binding energy of the molecules (atoms) of the liquid assuming simple cubic structure, inter-atomic distance of 2 \AA ($2 \times 10^{-10} \text{ m}$) and surface tension of 0.06 N/m . [7]

Ans:

$$\gamma = \frac{1}{4} \epsilon n N^s, \text{ where } n \text{ is number of neighbours and } N = 1/d^2 \text{ (} d \text{ is interatomic distance)}$$

$$\text{Hence } \epsilon = \frac{4\gamma d^2}{n} = \frac{4 * 0.061 * 4 * 10^{-20}}{6} = 0.16 * 10^{-20} \text{ J} = 0.01 \text{ eV}$$

(ii) Find surface tension γ of a liquid for which measured maximum droplet diameter in gravitational field of the Earth is 5 mm. The density of liquid is 1000 kg/m^3 . Assume spherical shape for the droplet at rest on a flat surface. [8]

Ans:

$F_G = mg$, and this is balanced by $F = \gamma l = \gamma 2\pi r$

$$m = \rho V = \rho \frac{4}{3} \pi r^3, \Rightarrow \gamma = \frac{2}{3} \rho g r^2 = \frac{2}{3} * 1000 * 9.8 * 6.25 * 10^{-6} \approx 0.04 \frac{N}{m}$$

(iii) Use the value of dissociation energy $3 * 10^{-21} \text{ J}$ and interatomic separation of 0.3 nm for simple cubic lattice to find:

(a) molar latent heat of melting, [5]

Ans: $\frac{1}{2} \epsilon (n_{\text{solid}} - n_{\text{liquid}}) N_A = 0.5(6-4) * 3 * 10^{-21} * 6.02 * 10^{23} = 1.8 * 10^3 \text{ J}$

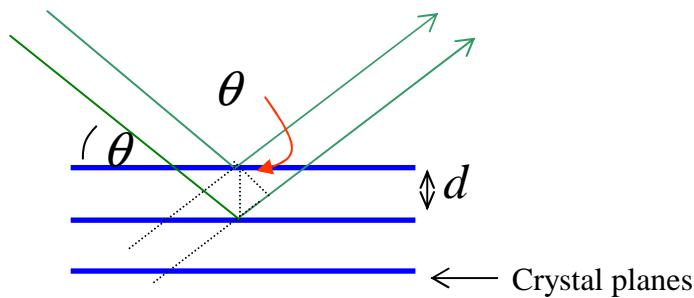
(b) bulk modulus [5]

Ans: $k = 4 n_{\text{solid}} \epsilon / d^3$, hence $k = 4 * 6 * 3 * 10^{-21} * 10^{30} / 27 = 2.7 * 10^9 \text{ J/m}^3$

(c) molar latent heat of evaporation [5]

Ans: $\frac{1}{2} \epsilon (n_{\text{liquid}} - n_{\text{gas}}) N_A \approx \frac{1}{2} \epsilon n_{\text{liquid}} N_A = 0.5 * 4 * 3 * 10^{-21} * 6.02 * 10^{23} = 3.6 * 10^3 \text{ J}$

B3. (i) Derive Bragg's law that relates is wavelength of x-rays (λ), inter-plane distance in crystal (d), and angle of incidence of x-rays (θ) (hint: use wave picture of x-rays together with geometric constructions of path difference of two waves and conditions of constructive interference). [8]



From condition of constructive interference: path difference = $n\lambda$, from geometric construction $n\lambda = 2d \sin \theta$

(ii) Interaction between two atoms of Ar is described by Lennard-Jones potential with $\epsilon = 0.02$ eV and atomic diameter $\sigma = 3.5$ Å. Find frequency $\nu = \frac{1}{2\pi} \sqrt{\frac{c}{m}}$ of atomic vibrations assuming small displacement of an atom from its equilibrium position (hint: use parabolic approximation for the interatomic potential close to equilibrium, $F(x) = -V''(a_0)x = -cx$) [10]

Ans:

$F(x) = -V''(a_0)x = -cx$, hence $c = V''(a_0)$, so we need to find a_0 . This can be done if we remember that $V'(a_0) = 0$.

Thus, we first differentiate LJ. to find a_0 , ($a_0 = 2^{1/6}\sigma$). We then differentiate LJ twice to find c .

$$a_0 = 3.81 \text{ \AA}$$

$$\begin{aligned} V''(a_0) &= 4\epsilon \left[156 \frac{\sigma^{12}}{r^{14}} - 42 \frac{\sigma^6}{r^{12}} \right]_{a_0} = 4\epsilon \left[156 \left(\frac{\sigma^{12}}{2^{14/6} \sigma^{14}} \right) - 42 \left(\frac{\sigma^6}{2^{8/6} \sigma^8} \right) \right] = \\ &= 4\epsilon \left[\frac{156}{2^{14/6} \sigma^2} - \frac{42}{2^{8/6} \sigma^2} \right] \approx 4\epsilon \left[\frac{156}{5\sigma^2} - \frac{42}{2.5\sigma^2} \right] = 4\epsilon \left[\frac{156 - 84}{5\sigma^2} \right] = 0.04 * 1.6 * 10^{-19} \text{ J} \left[\frac{72 * 10^{20} \text{ m}^{-2}}{5 * 11.56} \right] = \\ &= 0.797 \text{ J / m}^2 \end{aligned}$$

Ar molar mass is ~ 40 g/mol (see periodic table), hence atomic mass is that divided by Avogadro's number and equal to $\sim 7 * 10^{-26}$ kg. Thus the frequency is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{7.97 * 10^{25}}{7}} \approx \frac{10^5}{2\pi} \approx 1.6 * 10^4 \text{ Hz}$$

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(iii) Compare the pressure in the centre of the Earth with "interatomic" pressure. Consider Earth as a uniform sphere of density of $5,500 \text{ kg/m}^3$ and radius of earth of $6,400 \text{ km}$. For calculations of interatomic pressure between two atoms take binding energy to be 0.1 eV , and interatomic separation of 2 \AA (hint: in calculation of "interatomic" pressure consider that interatomic force is acting across region defined by atomic diameter). [10]

ANS: If we consider a simple approximation of Earth being a hard sphere of uniform density pressure can then be calculated by considering a small segment of the surface S of thickness dr :

Pressure exerted by this segment is then:

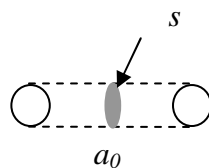
$$dP = \frac{dF}{S}, F = mg = mrS\rho \Rightarrow dP = \frac{gmS\rho dr}{S} = g\rho dr$$

$$\text{while } mg(r) = G \frac{mM}{r^2} \Rightarrow g(r) = \frac{GM}{r^2} = G\rho \frac{4}{3}\pi \frac{r^3}{r^2} = G\rho \frac{4}{3}\pi r$$

$$\text{and hence } dP = \rho G\rho \frac{4}{3}\pi r dr \Rightarrow P = \frac{4}{3}G\rho^2 \int_0^R r dr = \frac{2}{3}G\rho^2 R^2$$

$$\text{And hence } P = 6.673 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2} * 3.14 * (5500 \text{ kg m}^{-3})^2 * (6400 \text{ km})^2 * \frac{2}{3} \approx 14 * 30.25 * 41 * 10 \approx 1.7 * 10^{11} \text{ kg} * \text{m}^{-1} \text{ s}^{-2} = 1.7 * 10^{11} \text{ N/m}^2 = 1.7 * 10^{11} \text{ Pa}$$

Now, let's turn our attention to the "interatomic" pressure. We shall define it as a pressure that corresponds to the force acting between two isolated atoms that interact via LJ potential at low T.



Pressure can then be calculated as:

$$p = \frac{f}{s} = \frac{4f}{\pi\sigma^2}, \text{ where } \sigma \text{ is atomic diameter and}$$

$$f = f_{\text{attraction}} + f_{\text{repulsion}}$$

and we can find f for LJ from

$$\left. \frac{dV}{dr} \right|_{a_0} = 48\varepsilon \frac{\sigma^{12}}{a_0^{13}} - 24\varepsilon \frac{\sigma^6}{a_0^7} = 0 \Rightarrow f = 48\varepsilon \frac{\sigma^6}{a_0^7}$$

while

$$\sigma = \frac{a_0}{2^{1/6}} \Rightarrow f = \frac{24\varepsilon}{a_0} \Rightarrow p = \frac{2^{1/3} * 96\varepsilon}{\pi a_0^3} = \frac{1.26 * 96 * 1.6 \times 10^{-20} \text{ J}}{3.14 * 8 * 10^{-30} \text{ m}^3} = 7.7 * 10^{10} \text{ Pa}$$

So, even for a weak bond pressures are close.

B4.

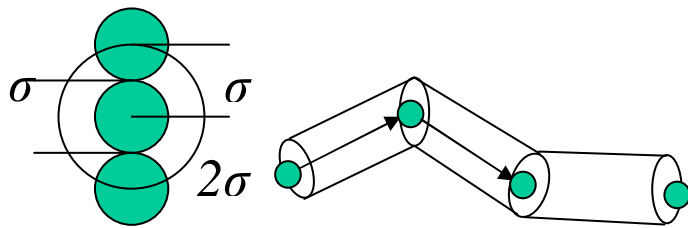
(i)

(a) Give a definition of *mean free path*. [2]

(b) Derive expression for *mean free path* (λ) considering that molecules of diameter σ collide elastically with each other within a volume with molecular concentration n . Write an expression for λ via thermodynamic parameters such as P , T and k_B . Calculate λ for air ($\sigma=0.3\text{nm}$) at $T=300 \text{ K}$ and $P=10^5 \text{ Pa}$ ($\sim 1 \text{ atm}$). [6]

Ans: We define the mean distance between collisions or *mean free path* as (distance travelled)/(number of collisions).

We will follow the progress of a single molecule as it collides with others moving through the gas. For simplicity we assume that the rest of the molecules are frozen in their positions. Thus if our lonely molecule travels distance l it will sweep an element of volume $\pi\sigma^2 l$ and if there are n molecules per m^3 then our molecule will collide with $\pi\sigma^2 ln$ of them. Hence:



$$\lambda = \frac{l}{\pi\sigma^2 nl} = \frac{1}{\pi\sigma^2 n} = \frac{k_B T}{P\pi\sigma^2}$$

and λ for air is $\approx 100\text{nm}$

(ii)

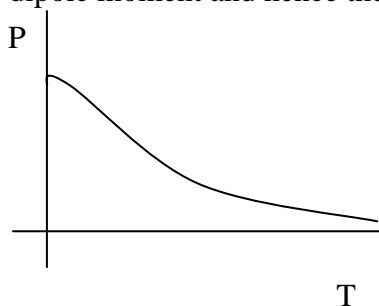
(a) Consider effect of an electric field on a gas (e. g. air) at standard pressure and temperature ($n \approx 3 \times 10^{25} \text{ m}^{-3}$) assuming that molecules of gas have an existing dipole moment due to charge separation (assume that dipole consists of two unit electronic charges separated by 1 \AA , dielectric permittivity of free space $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$). Calculate the value of induced total dipole moment P_d if dipoles were free to align along the field. [5]

(b) Calculate the corresponding net electric field E_d and compare to the typical field required to ionize air ($3 \times 10^6 \text{ V/m}$). Explain the result and suggest what the temperature-dependence of net dipole moment would look like. [5]

Ans: $p = \text{charge} * \text{separation} = 1.6 * 10^{-19} \text{ C} * 10^{-10} \text{ m} = 1.6 * 10^{-29} \text{ Cm}$

No field, no net momentum due to randomization. Switch on field and all dipoles are aligned, then $P_d = np$, and for a gas at STP $n \approx 3 * 10^{25} \text{ m}^{-3}$, hence $P_d \approx 5 * 10^{-4} \text{ C/m}^2$, and the field produced is $E_d = P_d / \epsilon_0 = 6 * 10^7 \text{ V/m}$

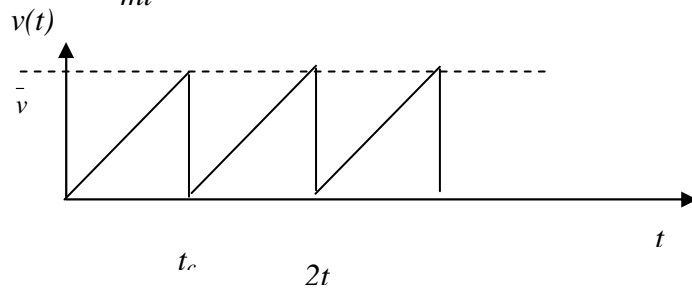
This would be more than enough to ionize most gases, but experiments show that this is not possible. The answer is temperature. Thermal motion distorts alignment of dipoles reducing the net dipole moment and hence the electric field.



(iii) A charge e in a conductor of length l subject to constant electric field E . Derive an expression for conductivity σ considering that a collision takes electron velocity u to 0 and that the current density is $j = ne\bar{u} = \sigma E$, where n is electron density (hint: draw the time dependence of the electron velocity to find \bar{u}). [12]

Ans: Electric field $E=V/l = \text{const}$, $F=e(V/l)=ma$ the drift velocity is then:

$$u(t) = at = \frac{eV}{ml}t \quad \text{The time dependence of the velocity is}$$



and $\bar{v} = \frac{eV}{ml}t_c$

Further $j = en\bar{v} = \frac{e^2Vn}{ml}t_c = \frac{e^2nt_c}{m} \left(\frac{V}{l} \right) = \sigma E$

$$\sigma = \frac{e^2nt_c}{m}$$

End of Examination Paper

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