
Examination
Fundamentals of Condensed Matter
(NWI-MOL431)

Monday, 28th October 2024, 08:30 – 11:30

Time allowed: **three hours**.

The exam consists of 6 questions divided over 3 parts:

Liquids, Solids I & Solids II.

Please hand in your answers to EACH PART on SEPARATE sheets.

Clearly write your name and student number on each sheet.

The marks in [] are only indicative of the weight given to each (sub)question.

A list of constants is included below.

List of constants

Elementary charge	e	$1.602 \times 10^{-19} \text{ C}$
Faraday's constant	F	$9.648 \times 10^4 \text{ C mol}^{-1}$
Boltzmann's constant	k_{B}	$1.381 \times 10^{-23} \text{ J K}^{-1} = 8.62 \times 10^{-5} \text{ eV K}^{-1}$
Planck's constant	h	$6.626 \times 10^{-34} \text{ J s}$
Speed of light	c	$3.0 \times 10^8 \text{ m s}^{-1}$
Atomic mass constant	m_{u}	$1.661 \times 10^{-27} \text{ kg}$
Avogadro's constant	N_{A}	$6.022 \times 10^{23} \text{ mol}^{-1}$
Gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Gravitational acceleration	g	9.807 m s^{-2}
Unit of energy		$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
Standard pressure	p^{\ominus}	$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 0.9869 \text{ atm}$
Unit of pressure		$1 \text{ atm} = 101.3 \text{ kPa}$

Part A: Liquids

1. The internal energy E is related to the canonical partition function Q and the configuration integral Z_N via:

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}, \quad \text{with} \quad Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} Z_N.$$

- a) Show that the internal energy can be written in terms of Z_N as [3]

$$E = \frac{3}{2} N k_B T + k T^2 \left(\frac{\partial \ln Z_N}{\partial T} \right)_{N,V}.$$

- b) i) Explain why the result from part 1a) implies that the mean potential energy is given by $\langle U \rangle = k T^2 \left(\frac{\partial \ln Z_N}{\partial T} \right)_{N,V}$. [2]

- ii) Given that $Z_N = \int \dots \int e^{-\beta U(\tau_1, \dots, \tau_N)} d\tau_1 \dots d\tau_N$, show that [6]

$$\langle U \rangle = \frac{\int d\tau_1 \dots \int d\tau_N U e^{-\beta U(\dots)}}{Z_N}.$$

Hint: change $\frac{\partial}{\partial T}(\dots)$ to $\frac{\partial}{\partial \beta}(\dots)$, with $\beta = 1/(k_B T)$.

- c) Assuming *pair-wise additivity*, the potential energy can be written as $U = \sum_{i>j}^N \phi_{ij}$, where $\phi(r_{ij}) = \phi_{ij}$ is the pair potential between particles i and j . Explain what *pair-wise additivity* means and how many terms there are in the summation. [2]

- d) The radial distribution function $g(r)$ can be expressed in terms of Z_N as

$$g(r) = V^2 \frac{\int d\tau_3 \dots \int d\tau_N e^{-\beta U(\dots)}}{Z_N}.$$

Using pair-wise additivity and this expression for $g(r)$ and starting from the result from part 1b-ii), derive the following expression for the mean potential energy in terms of the pair potential $\phi(r)$ and $g(r)$: [7]

$$\langle U \rangle = 2\pi \rho N \int_0^\infty r^2 \phi(r) g(r) dr.$$

2. The second virial coefficient is given by

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta \phi(r)} - 1 \right) r^2 dr,$$

where $\beta = 1/(k_B T)$, and $\phi(r)$ is the pair potential. The square-well pair potential $\phi(r)$ consists of a hard sphere (HS) part and an attractive (ATT) part and is given by:

$$\phi(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma \leq r \leq \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

with r the particle separation, σ the hard sphere diameter, and λ the range of the attractive interactions.

- a) Sketch $\phi(r)$ thereby clearly indicating σ , ϵ and λ . Also sketch the corresponding radial distribution function $g(r)$ at low densities, where $g(r) = e^{-\beta\phi(r)}$. [4]

- (b) i) Show that B_2 can be written as $B_2 = B_2^{HS} + B_2^{ATT}$, where [2]

$$B_2^{HS} = 2\pi \int_0^\sigma r^2 dr, \quad \text{and} \quad B_2^{ATT} = -2\pi (e^{\beta\epsilon} - 1) \int_\sigma^{\lambda\sigma} r^2 dr.$$

- ii) Calculate B_2^{HS} , explain its geometric interpretation and why it does not depend on the temperature. [3]

- (c) Use the low-density approximation for the radial distribution function, $g(r) = e^{-\beta\phi(r)}$, and the expression for the mean potential energy $\langle U \rangle$ [result of question 1d)],

$$\langle U \rangle = 2\pi\rho N \int_0^\infty r^2 \phi(r) g(r) dr,$$

to derive an expression for the mean potential energy in terms of B_2^{HS} and/or B_2^{ATT} and comment on your answer. [5]

- d) The compressibility equation is given by

$$1 + 4\pi\rho \int_0^\infty (g(r) - 1)r^2 dr = \rho k_B T \kappa_T,$$

where $\rho = \frac{N}{V}$ is the number density and κ_T the isothermal compressibility.

Again using that $g(r) = e^{-\beta\phi(r)}$, derive an expression for the isothermal compressibility in terms of B_2^{HS} and/or B_2^{ATT} and comment on your answer. [6]

3. a) In a scattering experiments the measured scattering intensity is proportional to the form factor $P(K)$ times the structure factor $S(K)$, i.e. $I(K) \propto P(K)S(K)$, with K the scattering vector and

$$S(K) = 1 + \rho \int (g(r) - 1) e^{i\vec{K}\cdot\vec{r}} d\vec{r}.$$

Briefly explain how the structure factor can be extracted from the total scattered intensity in an experiment. [2]

- b) Show that the isothermal compressibility κ_T can be measured from a scattering experiment by extrapolating the structure factor to $K \rightarrow 0$, in other words, show that $S(K \rightarrow 0) = \rho k_B T \kappa_T$. [3]

Part B: Solids I

4. a) At 5°C, iron (Fe) is found to show a bcc structure with a lattice parameter of 0.2866 nm. When heating iron above 912°C, its crystal structure changes to a face-centered cubic (fcc) crystal structure with a lattice parameter of 0.3571 nm. Calculate the atomic radius of iron in both the bcc and fcc structures. [3]
- b) Obtain the density of iron in the fcc structure as described in a). The atomic weight (molar mass) per 1 mole of Fe is 55.845 g. [3]
- c) Calculate the length of the unit cell edges and the unit cell volume when you describe the fcc structure of iron, as described in a), with a rhombohedral unit cell. [2]
- d) The symmetry matrix \mathbf{M} for a rotation θ around the z-axis is:

$$\mathbf{M} = \begin{vmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{vmatrix}.$$

Prove with matrices that point group $3/m$ (not used) is equivalent to point group -6 (which is being used) and show that point group $3/m$ (or -6) does not contain an inversion center. [6]

Hint: choose in both cases the rotation axes along the z-axis.

- e) For a perfect crystal the structure factor $F(hkl)$ determines the amplitude and phase of the diffracted beams::

$$F(hkl) = \sum_j f'_j(\theta) \cdot \exp[2\pi i(hx_j + ky_j + lz_j)] = |F(hkl)| \cdot \exp[i\varphi(hkl)],$$

where the sum is over all atoms in the unit cell, x_j , y_j and z_j are the positional coordinates of the atoms and $f'_j(\theta)$ is the scattering factor of the j -th atom. hkl are the indices of the lattice planes. Show that for an fcc structure, like Fe at high temperature, the structure factor has values different from zero only for $h, k, l =$ all even or $h, k, l =$ all odd. [6]

- f) The d -spacing in a triclinic crystal is given by:

$$\frac{1}{d^2} = \frac{1}{V^2} \begin{pmatrix} h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma \\ + 2hkabc^2(\cos \alpha \cos \beta - \cos \gamma) \\ + 2kla^2 bc(\cos \beta \cos \gamma - \cos \alpha) \\ + 2hlab^2 c(\cos \alpha \cos \gamma - \cos \beta) \end{pmatrix},$$

with

$$V = abc (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}.$$

Consider a crystal with a hexagonal unit cell with $a = 10 \text{ \AA}$ and $c = 20 \text{ \AA}$. Using the Bragg equation, $2d \sin \theta = n\lambda$, calculate the Bragg angle θ for the first and second order reflections from the lattice planes (100), (200), (002) and (111), using an X-ray wavelength $\lambda = 1.54 \text{ \AA}$, for this crystal. [6]

Part C: Solids II

5. Silicon has a band gap (E_g) of 1.11 eV. The electrical conductivity of intrinsic silicon at room temperature is $\sigma_i = 4 \times 10^{-4} \Omega^{-1}\text{m}^{-1}$ and its electron and hole mobilities are $\mu_e = 0.14 \text{ m}^2/(\text{V s})$ and $\mu_h = 0.05 \text{ m}^2/(\text{V s})$. The atomic weight and density at room temperature of silicon are respectively $M_{\text{Si}} = 28.09 \text{ g/mol}$ and $\rho_{\text{Si}} = 2.33 \text{ g/cm}^3$.
- Calculate for silicon the room temperature conductivity carried by the holes. [2]
 - In intrinsic semi-conductors the conductivity is given by $\sigma_i = \sigma_{i0} \exp[-E_g/(2k_B T)]$. Calculate the conductivity of silicon at 150°C. [3]
 - Calculate the donor density that should minimally be introduced in order to increase the room temperature conductivity to $150 \Omega^{-1}\text{m}^{-1}$. [2]
 - Explain why no hole is generated by the electron excitation of the donor impurity. [1]
 - Show that the extrinsic conduction in a semiconductor is a structure sensitive property. [2]
6. Suppose that a Si p-n junction is produced by MOCVD growth of a thin single crystal p-type Si layer on top of an n-doped single crystal layer.
- Would you expect the formation of misfit dislocations at the interface between these two types of Si? [1]
 - Calculate the maximum light induced current that can be generated in an Si diode with a light sensitive surface of 1 cm^2 if it is illuminated with 400 nm monochromatic light with an intensity of 300 W/m^2 . The photon energy is given by $E_p = hc/\lambda$. [3]

If the Si photodiode is not thick enough to absorb all the light in a single pass, this can be remedied by deposition of a metallic layer at the rear side of the diode to reflect the non-absorbed light back into the semiconductor diode.

- Which techniques can be applied to deposit such a reflective metal coating? [2]
- Without knowing the exact reflectivity of the metals would it be better to apply a silver or a copper coating in order to obtain a maximum current from the diode? [2]
- Explain how the transmission loss in a thin photodiode can also be resolved by the use of another semiconductor material instead of Si. [2]