

Study Guide

Fundamentals of Condensed Matter

(NWI-MOL431) 2026/2027

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Recommended course material

- Book: Physical Chemistry; P.W. Atkins, Oxford University Press, 11th edition (basic physical chemistry)
- Book: Statistical Mechanics by McQuarrie
- Book: Introduction to Statistical Thermodynamics by Hill
- Book: The basics of crystallography and diffraction by Hammond, Oxford University Press, 4th edition
- Lecture handouts
- All information will be available via in **Brightspace** and/or **www.dullenslab.com/teaching/fcm**

Aim

- After this course, the students (i) has a good understanding of the basic thermodynamics and statistical mechanics (of interacting systems), (ii) can explain and apply concepts from liquid state theory to describe the structure and thermodynamics of liquids, (iii) is able to explain and apply fundamental concepts of crystal structures and diffraction, and (iv) can relate the physical properties of solids to their crystal structure.

Organisation

- **Lectures**

During the lectures (Monday, 15:30 – 17:15, and Thursday, 8:30 – 10:15, HG00.086) the main contents of this Fundamentals of Condensed Matter course will (obviously) be discussed and explained. Please bring a notebook (and an active mindset) to the lectures so that you can write (and think) along. Note that the lectures and the suggested literature supplement each other, and some topics will be presented differently than in the books.

- **Problem Classes**

The problems for the problem classes (Thursday, 10:30 – 12:15, HG03.085) will appear online (**www.dullenslab.com/teaching/fcm** and/or **Brightspace**); answers will be available online after the problem classes.

- **Examination**

The evaluation will consist of a 3-hour written exam. **Graphical calculators are NOT allowed during the exam (regular ones are).**

- **Video recordings**

The lectures are not recorded.

Contents of Fundamentals of Condensed Matter

Lecture synopsis

1. Basic thermodynamics and statistical mechanics
2. Second virial coefficient
3. Structure of liquids
4. Complex fluids
5. Ordering and bonding in solids
6. Crystallographic symmetry
7. Diffraction techniques
8. Crystal engineering
9. Crystal growth and defects
10. Material properties
11. Tuning properties in semiconductors

Problem set 1 – Liquids

Problem 1

Consider a process in which n moles of a perfect mono-atomic gas expands isothermally and reversibly from volume V_1 to volume $V_2 = 2V_1$.

- a) What is the change in internal energy for this process?
- b) Starting from the thermodynamic definition of entropy $dS = \frac{dq_{rev}}{T}$ show that the entropy change ΔS for this reversible expansion is given by

$$\Delta S = nR \ln 2.$$

- c) Write the answer to part b) in the form of Boltzmann's statistical definition of entropy, $S = k_B \ln \Omega$, hence, show that $\frac{\Omega_2}{\Omega_1} = 2^N$. How does the number of possible ways to realise a given configuration change due to the expansion?
- d) From the fundamental equation for the Helmholtz free energy, derive the following Maxwell-relation

$$\left(\frac{\partial S}{\partial V} \right)_{T,n} = \left(\frac{\partial p}{\partial T} \right)_{V,n}.$$

and use this to calculate the entropy change for an isothermal expansion of a perfect monatomic gas from volume V_1 to volume $V_2 = 2V_1$ (cf part b).

Problem 2

- a) Starting from the Gibbs-Duhem equation, $d\mu = -S_m dT + V_m dP$, derive the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}.$$

- b) Starting from the Clapeyron equation, clearly stating any approximations, derive the Clausius-Clapeyron equation for the vapour pressure of a liquid

$$\frac{d \ln p}{dT} = \frac{\Delta_{vap} H}{RT^2}.$$

- c) The enthalpy of vaporization of water is 44.0 kJ mol^{-1} . Estimate the vapour pressure of water at 120°C .

Problem 3

The Van der Waals equation of state for one mole ($n = 1$) is given by

$$p = \frac{RT}{V - b} - \frac{a}{V^2}.$$

- a) Explain the physical significance of the Van der Waals parameters a and b .

The critical point is defined by the conditions

$$\left(\frac{\partial p}{\partial V} \right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0.$$

- b) Apply the above conditions to the Van der Waals equation state to find the critical volume $V_c = 3b$, temperature $T_c = \frac{8a}{27Rb}$ and pressure $p_c = \frac{a}{27b^2}$.
- c) Due to intermolecular interactions carbon dioxide cannot be treated as a perfect gas, but does obey the Van der Waals equation. Given that $a = 0.361 \text{ Jm}^3\text{mol}^{-2}$ and $b = 42.9 \cdot 10^{-6} \text{ m}^3\text{mol}^{-1}$ for CO_2 , calculate the V_c , T_c and p_c for carbon dioxide. How does it compare to the actual critical temperature (304.2 K) and critical pressure (72.9 atm) of CO_2 ?

The Van der Waals equation of state can also be written in terms of a virial expansion (for $n = 1$ mole):

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \approx \frac{RT}{V} \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V} + \dots \right].$$

- d) Calculate the Boyle temperature and explain why the Boyle temperature is generally higher than the critical temperature for a given gas.

Problem 4

- a) Explain briefly what is meant by a canonical ensemble, and why it is a useful concept in statistical mechanics.
- b) State how the internal energy (E) and the Helmholtz free energy (A) are related to the canonical partition function $Q \equiv Q(N, V, T)$.
- c) The canonical partition function for an interacting gas is given approximately by

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N \exp \left[\frac{aN^2}{V k_B T} \right]$$

where a and b are positive constants.

Show that $p = k_B T (\partial \ln Q / \partial V)_{N, T}$ and, hence, obtain an expression for the pressure of the gas. Comment on your result.

- d) Show that the internal energy per atom is given by

$$\frac{E}{N} = \frac{3}{2} k_B T - a \frac{N}{V}.$$

and comment on the physical interpretation of the fact that this result does not depend upon b .

Problem 5

- a) Show that the molecular partition function for a harmonic oscillator, for the case that the zero-point energy of the oscillator has been defined as zero, is given by

$$q_{vib} = \left(1 - e^{-h\nu/k_B T}\right)^{-1},$$

where the ν is the vibrational frequency (in s^{-1}). Note that $1 + x + x^2 + \dots = (1 - x)^{-1}$.

- b) The Einstein model of a solid comprises of N atoms free to undergo independent harmonic vibrational motion along the x , y and z directions with the same Einstein frequency ν_E . Show that the Einstein model of such a 3D solid with N atoms yields the following expression for internal energy

$$E(T) = 3Nh\nu_E \left(e^{h\nu_E/k_B T} - 1\right)^{-1}.$$

- c) Obtain an expression for the molar heat capacity of the solid at constant volume, $C_V = (\partial E / \partial T)_V$, and show that, if written in terms of the Einstein temperature $\theta_E = h\nu_E/k_B$, the following result is obtained

$$C_V(T) = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \left[= 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{-\theta_E/T}}{(1 - e^{-\theta_E/T})^2} \right].$$

Note that this is another example of the *Law of Corresponding States*: if plotted as a function of the reduced temperature, T/θ_E , the heat capacity C_V of various crystals will superimpose, just as we have seen in lecture 1 for the Van der Waals equation of state.

Problem 6

A perfect monatomic gas in thermal equilibrium occupies a vertical cylinder of height h and cross-sectional area A , in a uniform gravitational field with characteristic acceleration g .

- Find an expression for the classical molecular partition function of the gas. Note that the potential energy for a gas molecule equals mgz .
- Show that in the limit of $mg h/k_B T$ becoming very small (i.e. in the limit of no gravity), the classical molecular partition function of a perfect gas is recovered.
- Estimate the height h at which this simplification breaks down for xenon.

Note that

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2) dx = \sqrt{\frac{\pi}{\alpha}}$$

Problem set 2 – Liquids

Problem 7

The classical configuration integral is given by

$$Z_N = \int \dots \int e^{-\beta U(\tau_1, \dots, \tau_N)} d\tau_1 \dots d\tau_N,$$

where $U(\tau_1, \dots, \tau_N)$ is the total potential energy and $\beta = 1/(k_B T)$.

- Explain what is meant by *pair-wise additivity* and give the corresponding expression for U in terms of the pair potential between particles i and j , $\phi(r_{ij}) = \phi_{ij}$.
- Use your above expression for U in terms of ϕ_{ij} within the pair-wise additivity approximation together with the definition of the Mayer f -function, $f_{ij} \equiv e^{-\beta \phi_{ij}} - 1$, to show that Z_N can be written as

$$Z_N = \int \dots \int \prod_{i>j}^N (1 + f_{ij}) d\tau_1 \dots d\tau_N.$$

- Explain the significance of the Mayer f -function in performing the integrals in Z_N . Include in your answer a sketch of a realistic/reasonable pair potential ϕ_{ij} and the corresponding Mayer f -function f_{ij} .

Problem 8

For a monatomic system the second virial coefficient is given explicitly by

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

where $\phi(r)$ is the intermolecular pair potential and $\beta = 1/(k_B T)$.

- Sketch the square well potential defined as follows:

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

- Find an expression for the second virial coefficient for this potential.
- The properties of Ar gas can be described using the square well potential with $\sigma = 3.067 \text{ \AA}$, $\lambda = 1.70$ and $\epsilon/k_B = 93.3K$. Calculate the predicted value of the Boyle temperature.

Problem 9

The pair potential between molecules forming an imperfect gas can be described by the following interaction potential

$$\phi(r) = \begin{cases} \infty & r < \sigma \\ -\frac{A}{r^6} & r \geq \sigma \end{cases}$$

where $A = 1.11 \times 10^{-78} \text{ J m}^6$ is an interaction parameter and $\sigma = 0.356 \text{ nm}$ is the hard sphere diameter.

- a) Sketch the interaction potential $\phi(r)$ and calculate the depth of the potential energy at contact (i.e. at $r = \sigma$).
- b) Using that $\phi \ll k_B T$ for $r \geq \sigma$, show that the second virial coefficient $B_2(T)$ for this potential may be written as

$$B_2(T) = 2\pi \int_0^\sigma r^2 dr + 2\pi \int_\sigma^\infty \frac{\phi(r)}{k_B T} r^2 dr$$

- c) The imperfect gas under consideration obeys the Van der Waals equation of state, which can also be written in terms of a virial expansion

$$p = \frac{Nk_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2 \approx k_B T \left[\rho + \left(b - \frac{a}{k_B T} \right) \rho^2 + \dots \right]$$

Combine the answer to (b) and the above virial expansion to show that the van der Waals parameters are given by

$$a = -2\pi \int_\sigma^\infty \phi(r) r^2 dr \quad b = 2\pi \int_0^\sigma r^2 dr$$

- d) Hence, calculate a and b and explain their physical significance.

Problem 10 – Extra

Consider a Lennard-Jones gas for which the pair potential is

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

with ϵ the depth of the potential well and σ the particle diameter.

- a) By transforming the integration variable from r to dimensionless distance $y = r/\sigma$ and defining the dimensionless temperature $T^* = k_B T/\epsilon$, show that

$$B_2(T)/\sigma^3 = -2\pi \int_0^\infty \left[\exp \left(-\frac{4}{T^*} [y^{-12} - y^{-6}] \right) - 1 \right] y^2 dy$$

Hence, the dimensionless second virial coefficient for a Lennard-Jones gas $B_2^*(T^*) = B_2(T)/\sigma^3$ is a function *solely* of the dimensionless temperature T^* .

- b) Now assume that the higher order virial coefficients for a Lennard-Jones gas $B_n^*(T^*) = B_n(T)/\sigma^{3(n-1)}$ are likewise functions solely of T^* , and define the dimensionless number density ρ^* and the dimensionless pressure p^* by:

$$\rho^* = \rho \sigma^3 \quad p^* = \frac{p \sigma^3}{\epsilon}$$

Show from the virial expansion $p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$ that the equation of state of a Lennard-Jones gas is a universal function of (p^*, ρ^*, T^*) . In other words, *different Lennard-Jones systems with different parameters σ and ϵ all have the same equation of state expressed in the dimensionless quantities (p^*, ρ^*, T^*)* . This is an (other) example of the ‘law of corresponding states’.

Problem 11

In this problem we will obtain the expression for the radial distribution function $g(r)$ in terms of the configuration integral Z_N (derived in lecture 4) in a slightly different way.

- (a) Consider a one-component fluid. The probability that any particle is in $d\tau_1$ at $\mathbf{r}_1$ and any second particle in $d\tau_2$ at $\mathbf{r}_2$, irrespective of the positions of the other $N - 2$ particles, can also be expressed in terms of the pair correlation function $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$:

$$\rho^2 g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2. \quad (\rho = N/V) \quad \text{Eq. 1}$$

What would the above probability be if all the particles were *independent* of each other? In other words, what would the value of $g^{(2)}$ be in this case and explain that the factor $g^{(2)}$ thus corrects for the “non-independence”, i.e. the *correlations* between the particles.

Note that for isotropic and homogeneous systems such as liquids and gases, $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ only depends on the relative distance between particles 1 and 2: $g^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) = g(r)$, which is of course the radial distribution function.

- b) As we have seen in lecture 4, the probability that particle 1 is in $d\tau_1$ at $\mathbf{r}_1$ and particle 2 is in $d\tau_2$ at $\mathbf{r}_2$, irrespective of the positions of the other $N - 2$ particles, is:

$$\frac{\int d\tau_3 \cdots \int d\tau_N e^{-\beta U(\dots)} d\tau_1 d\tau_2}{Z_N}. \quad \text{Eq. 2}$$

Explain that the probability that *any* particle is in $d\tau_1$ and *any* second particle in $d\tau_2$, irrespective of the positions of the other $N - 2$ particles, is the above probability multiplied by $\frac{N!}{(N-2)!}$.

- c) Show that

$$\frac{N!}{\rho^2 (N-2)!} = V^2 \left[1 - \left(\frac{1}{N} \right) \right]. \quad \text{Eq. 3}$$

- d) Combine Eqs. 1 and 3 from parts a) and c) with your answer to part b) to obtain the expression for the radial distribution function $g(r)$ in terms of the configuration integral Z_N (which was also derived in lecture 4):

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

Problem 12

The compressibility equation is given by

$$1 + 4\pi\rho \int_0^\infty h(r)r^2 dr = \rho k_B T \kappa_T, \quad \text{Eq. 1}$$

where $\rho = \frac{N}{V}$ is the number density, $h(r) \equiv g(r) - 1$ the total correlation function and $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$ the isothermal compressibility.

- (a) Show that the isothermal compressibility can be rewritten as

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T.$$

The second virial coefficient is given by

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

where $\phi(r)$ is the interaction pair potential as a function of the separation r and $\beta = 1/(k_B T)$.

- (b) In the limit of small ρ we can assume that the radial distribution function $g(r) = \exp(-\phi(r)\beta)$. Use this to show that in the low density limit the compressibility equation can be written in terms of B_2 as

$$1 - 2\rho B_2 = k_B T \left(\frac{\partial \rho}{\partial p} \right)_T.$$

- (c) Show that for small ρ this can be approximated as

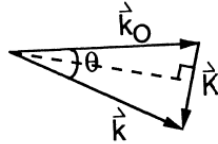
$$\left(\frac{\partial p}{\partial \rho} \right)_T = k_B T (1 + 2\rho B_2 + \dots).$$

and, hence, obtain an expression for the pressure. Comment on your answer.

Problem set 3 – Liquids

Problem 13

- a) Show that magnitude of the scattering vector is given by $K \equiv |\vec{K}| = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ using the figure below.



$$|\vec{k}| = |\vec{k}_0| = k$$

- b) Calculate the scattering angle corresponding to a K -value of 0.015 nm^{-1} for light scattering ($\lambda = 532 \text{ nm}$) and X-Ray scattering ($\lambda = 0.15 \text{ nm}$).
- c) The scattered intensity is proportional to the form factor $P(K)$ times the structure factor $S(K)$, i.e. $I(K) \propto P(K)S(K)$. Briefly explain how the structure factor can be extracted from the total scattered intensity in an experiment.
- d) Sketch how the radial distribution functions and structure factors for a hard sphere system change as the number density ρ is increased.

Problem 14

The Ornstein-Zernike equation can be written as

$$h_{12} = c_{12} + \rho \int d\tau_3 c_{13} h_{32}.$$

- a) Explain the meaning of each symbol, also taking into account the subscripts. Give physical interpretations of h and c . What is meant by the term 'closure relation'?
- b) Explain the basis for the Ornstein-Zernike equation in terms of direct and indirect interactions using a sketch.
- c) The Fourier transform of the Ornstein-Zernike equation reads

$$\hat{h}(K) = \hat{c}(K) + \rho \hat{c}(K) \hat{h}(K).$$

Show that this can be rearranged to

$$1 + \rho \hat{h}(K) = \frac{1}{1 - \rho \hat{c}(K)},$$

and explain the experimental significance of the left-hand side of this equation.

Problem 15

The compressibility equation is given by

$$1 + 4\pi\rho \int_0^\infty h(r)r^2 dr = \rho k_B T \kappa_T, \quad \text{Eq. 1}$$

where $\rho = \frac{N}{V}$ is the number density, $h(r) \equiv g(r) - 1$ the total correlation function and $\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T$ the isothermal compressibility.

- a) Sketch the total correlation function $h(r)$ for a *very dilute* fluid of hard spheres. The hard spheres have a diameter σ .
- b) The structure factor for an isotropic fluid is given by

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

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 $S(K \rightarrow 0) = \rho k_B T \kappa_T$.

- c) For isotropic systems the structure factor can also be written in spherical coordinates:

$$S(K) = 1 + \frac{4\pi\rho}{K} \int_0^\infty h(r) \sin(Kr) r dr.$$

Derive the following analytic expression for $S(K)$ for a *very dilute* gas of hard spheres.

$$S(K) = 1 + \frac{4\pi\rho}{K^2} \left(\sigma \cos(K\sigma) - \frac{\sin(K\sigma)}{K} \right).$$

Hints: use your result from part a) and integration by parts.

- d) Find the limit of $S(K)$ as $\sigma \rightarrow 0$, and then calculate the equation of state (the pressure) using the result from part b), i.e. via the compressibility κ_T . Comment on your answers.

Problem 16

In the dilute limit ($\rho \rightarrow 0$), the radial distribution function $g(r)$ is related to the pair potential $\phi(r)$ via

$$g(r) = \exp(-\beta\phi(r)).$$

Sketch the pair potentials and corresponding radial distribution functions for the following systems at low number density ρ :

- a) perfect gas,
- b) hard sphere gas (diameter σ),
- c) attractive hard sphere gas (diameter σ).

Problem 17

The internal energy E is related to the canonical partition function Q via

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

Here Z_N is the configuration integral Z_N .

a) Use the above equations to show that

$$E = \frac{3}{2} N k_B T + k_B T^2 \left(\frac{\partial \ln Z_N}{\partial T} \right)_{N,V} \quad (= E_{kin} + \langle U \rangle).$$

b) From part a), we see that $\langle U \rangle = k T^2 \left(\frac{\partial \ln Z_N}{\partial T} \right)_{N,V}$. Combine this with $Z_N = \int \dots \int e^{-\beta U(\tau_1, \dots, \tau_N)} d\tau_1 \dots d\tau_N$ to show that

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

c) Next, using pairwise additivity, $U = \sum_{i>j} \phi_{ij}$, derive the following expression for the mean potential energy in terms of the pair potential $\phi(r)$ and the radial distribution function $g(r)$:

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

d) Finally, using that in the dilute limit $g(r) = \exp(-\beta\phi(r))$, calculate the average potential energy for the square well potential,

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

Comment on the result you obtain for the case that $\lambda = 1$.