# Imperial College London
# BSc/MSci EXAMINATION June 2012

*This paper is also taken for the relevant Examination for the Associateship*

# THERMODYNAMIC AND STATISTICAL PHYSICS

## For 2nd-Year Physics Students

Friday, 15th June 2012: 10:00 to 12:00

*Answer ALL parts of Section A, ONE question from Section B and ONE question from Section C.*
*Marks shown on this paper are indicative of those the Examiners anticipate assigning.*

**General Instructions**

Complete the front cover of each of the 4 answer books provided.

If an electronic calculator is used, write its serial number at the top of the front cover of each answer book.

USE ONE ANSWER BOOK FOR EACH QUESTION.

Enter the number of each question attempted in the box on the front cover of its corresponding answer book.

Hand in 4 answer books even if they have not all been used.

**You are reminded that Examiners attach great importance to legibility, accuracy and clarity of expression.**

# SECTION A

**1.** (i) Are the following variables intensive or extensive:

(a) pressure,

(b) entropy,

(c) specific Gibbs function.

[2 marks]

(ii) An object undergoes a reversible heat flow at constant pressure, as a result of which its temperature changes from $T_0$ to $T_1$. Show that the entropy of the object changes by

$$\Delta S = C_P \ln\left(\frac{T_1}{T_0}\right)$$

where $C_P$ is the constant pressure heat capacity (assumed to be constant).

Calculate the entropy change of 0.3 kg of water cooling from 90°C to 30°C at constant pressure.

[The constant pressure specific heat of water is $4.18 \times 10^3$ J K$^{-1}$ kg$^{-1}$.]

[5 marks]

(iii) Enthalpy is defined as: $H = U + PV$. Use the fundamental equation of thermodynamics to show that $dH = TdS + VdP$.

By writing $H$ as a function of an appropriate pair of state variables, obtain expressions for $T$ and $V$ in terms of partial derivatives of $H$. Hence show that

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P .$$

[5 marks]

[Total 12 marks]

**2.** (i) Define the concepts of grand canonical, canonical and microcanonical ensembles. [3 marks]

(ii) If two thermodynamic systems A and B, with the same temperature but different chemical potentials such that $\mu_A < \mu_B$, are brought into contact so they can exchange particles and energy, what happens? [1 mark]

(iii) Write down the distribution function for energy states that is appropriate for the case of a photon gas. What is the chemical potential in this case? [2 marks]

(iv) Write down the Gibbs entropy for a canonical ensemble, defining the terms you use. [2 marks]

[Total 8 marks]

## SECTION B

**3.** (i) A reversible heat engine operates in a Carnot cycle. One cycle consists of the following four stages:

A $\rightarrow$ B: isothermal expansion, heat $Q_H$ from hot reservoir at $T_H$,

B $\rightarrow$ C: adiabatic expansion,

C $\rightarrow$ D: isothermal compression, heat $Q_C$ to cold reservoir at $T_C$,

D $\rightarrow$ A: adiabatic compression.

Sketch this cycle on a $TS$ diagram, indicating the points A, B, C and D, and the temperatures $T_H$ and $T_C$. [5 marks]

(ii) Indicate clearly on separate $TS$ diagrams the areas corresponding to $Q_H$ and $Q_C$, and, hence, show that $Q_H/Q_C = T_H/T_C$. [2 marks]

(iii) The Carnot engine is now run in reverse and used as a heat pump. Defining the coefficient of performance of such a device, $\omega^P$, as the heat out of the device in one cycle divided by the work done in one cycle, show that $\omega^P_{Carnot} = T_H/(T_H - T_C)$.

[4 marks]

(iv) The Carnot heat pump is used to keep the interior of a building at 21°C. The heat is extracted from the ground at 5°C, and the building is losing heat at a rate 20 kW. Calculate:

(a) the coefficient of performance of the heat pump, and,

(b) the required power that the heat pump motor must deliver. [4 marks]

(v) Consider a real heat pump which in one cycle extracts heat $Q_C$ from the ground at temperature $T_C$ and delivers heat $Q_H$ to a building at at temperature $T_H$. Use the Clausius inequality to show that $Q_C < Q_H T_C/T_H$, and, hence, that the coefficient of performance is less than that of the Carnot heat pump [see part (iii), above].

Briefly explain how the heat pump with the lower coefficient of performance can maintain the building's temperature while extracting less heat from the ground.

[5 marks]

[Total 20 marks]

**4.** (i) Write down the fundamental equation of thermodynamics, identifying all the terms in it. [1 mark]

(ii) The internal energy of an ideal gas is given by $U = \frac{n_d}{2} N k_B T$, where $n_d$ = the number of degrees of freedom of the molecules (do not attempt to prove this equation).

Using the fundamental equation of thermodynamics, show that the entropy of a fixed mass of monatomic ideal gas is given by

$$S = S_0 + \frac{3}{2} N k_B \ln T + N k_B \ln V \ ,$$

where $S_0$ is a constant. [3 marks]

(iii) A monatomic ideal gas is initially at a temperature of 293 K, and a pressure of $10^5$ Pa, and has a volume of 0.1 m$^3$. Calculate:

(a) the number of molecules, and

(b) the internal energy of the gas. [2 marks]

(iv) The ideal gas referred to in part (iii) undergoes adiabatic free expansion to a volume of 0.5 m$^3$.

(a) Is this process reversible?

(b) What is the internal energy of the gas at the end of this process?

(c) What is the temperature of the gas at the end of this process?

(d) Calculate the entropy change of the universe due to this process.

[6 marks]

(v) Instead of undergoing adiabatic free expansion, the ideal gas referred to in part (iii) undergoes a reversible, isothermal expansion at $T$ = 293 K to a volume of 0.5 m$^3$.

(a) What is the internal energy of the gas at the end of this process?

(b) Calculate the work done *by* the gas in this process.

(c) What is the entropy change of the universe due to this process? [4 marks]

(vi) Briefly discuss the connection between entropy change and energy degradation, illustrating your discussion with the situations described in parts (iv) and (v).

[4 marks]

[Total 20 marks]

## SECTION C

**5.** (i) Write down the Fermi-Dirac distribution function, $f(\epsilon)$, defining all the terms you use. Define also the Fermi energy $\epsilon_F$ and Fermi temperature $T_F$. [3 marks]

(ii) What is the maximum value that $f(\epsilon)$ can take? What physical principle does this embody? Sketch the Fermi-Dirac distribution at $T = 0$ and a higher temperature. [4 marks]

(iii) The density of states of a "particle in a box" model of a 3D gas is given by

$$g(\epsilon)d\epsilon = \frac{DV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}d\epsilon.$$

Here, $m$ is the particle mass and $V$ is the volume of the box. What is the value of the degeneracy factor $D$ for the case of electrons in a metal? Why? [1 mark]

(iv) By integrating the number of particles over all energies for the case of $T = 0$, show that the Fermi temperature is given by

$$T_f = \left(\frac{6N\pi^2}{DV}\right)^{2/3} \frac{\hbar^2}{2mk_B}.$$

[4 marks]

(v) In copper, the number density of free electrons is $8.5 \times 10^{22}$ cm$^{-3}$. Calculate $T_F$. Comment on what this result means for the distribution of electrons between energy levels at room temperature. [2 marks]

(vi) For the case of zero temperature, derive an expression for the internal energy of the free electrons

$$U = \int_0^\infty g(\epsilon)f(\epsilon)\epsilon d\epsilon.$$

Show that

$$U = \frac{3}{5}N\epsilon_F.$$

[4 marks]

(vii) The pressure of a Fermi gas is related to the internal energy as $P = 2U/3V$. Calculate a value for the pressure of the free electrons in copper. How does this compare to atmospheric pressure? Why do the electrons not just evaporate out of the metal? [2 marks]

[Total 20 marks]

**6.** (i) Write down the Boltzmann definition of entropy $S$ in terms of the multiplicity $\Omega$ and describe the physical meaning of $\Omega$. [2 marks]

(ii) Consider a system of $N$ identical, distinguishable, classical particles. Each particle can occupy energy states $\epsilon_j$. Explain why, if there are $n_j$ particles in state $j$, then

$$\Omega = \frac{N!}{\prod_j n_j!}.$$

[4 marks]

(iii) The equilibrium distribution of particles between levels is $n_j = exp(\alpha - \beta\epsilon_j)$.
What is $\beta$? Define the partition function $Z$ and hence determine the constant $\alpha$. [4 marks]

(iv) Using your definition of $S$ and the above expression for $\Omega$, show that, assuming large $N$ and $n_j$,

$$S = Nk_B \ln Z + \frac{U}{T}$$

where $U$ is the total internal energy.
You may use Stirling's approximation for large $N$:

$$\ln N! = N \ln N - N.$$

[7 marks]

(v) Hence, given the thermodynamic definition of the Helmholtz free energy,

$$F = U - TS,$$

derive the "bridge equation" which defines $F$ in terms of the partition function. Why is this a useful result? [3 marks]

[Total 20 marks]