

# UNIVERSITY OF SURREY®

Faculty of Engineering and Physical Sciences

Department Of Physics

BSc and MPhys Undergraduate Programmes in Physics

## Module PHY2063; 15 credits

### Energy and Entropy

FHEQ Level 5 (Year 2) Examination

Time allowed: 1.5 hours

Semester 1 2012/13

Answer **TWO** questions only

Each question carries 20 marks.

Where appropriate the mark carried by an individual part of a question is indicated in square brackets [ ].

*Additional Materials:*

Department of Physics Formulae Booklet

Candidates may use only calculators which are non-programmable and with no alphanumeric memory. Calculators approved for use in the Physics Department are:

Casio: FX-82 Series, FX-83 Series, FX-85 ES, FX-115MS, 115W, 115S and FX-570W

Sharp: EL-531 LH

Texas Instruments: TI-30X

Tandy: EC-4031, EC-4032

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1.

(a)

- (i) State the second law of thermodynamics in terms of the entropy.

**[3 marks]**

- (ii) Boltzmann's expression for entropy is given by
- $S = k_B \ln W$
- . Explain what is meant by
- $W$
- .

**[3 marks]**

(b)

- (i) A crystal has
- $N$
- lattice sites filled with
- $N$
- atoms of type
- $A$
- . If
- $m$
- of these atoms are replaced by atoms of type
- $B$
- find an expression for
- $W$
- . Hence, by using Stirling's approximation, an expression for the entropy of the crystal.

*[Note: Stirling's approximation is given by  $\ln N! = N \ln N - N$ ]***[6 marks]**

- (ii) If we denote the fraction of atoms of type
- $B$
- as
- $x$
- , then the Helmholtz free energy per site (up to an additive constant) can be written as

$$f = \frac{F}{N} = \epsilon x + k_B T [x \ln x + (1 - x) \ln(1 - x)],$$

where  $\epsilon$  is the energy required to replace an atom of type  $A$  with type  $B$ .Show that the equilibrium value for  $x$  obeys the expression

$$\frac{x}{1 - x} = e^{-\epsilon/(k_B T)}$$

**[4 marks]**

- (c) If lead is placed in contact with tin, then some of the tin atoms are dissolved in the lead by replacing them on the lattice. At
- $300K$
- , 3% of the lead atoms are replaced by tin. Find the energy required to replace a lead atom with a tin atom, and hence estimate the solubility of tin in lead at
- $100K$
- .

**[4 marks]**

2.

- (a) Give an equation for the partition function,  $Z$ , defining the symbols used. State how  $Z$  is used in the calculation of probabilities of the occupation of an energy state, and the Helmholtz free energy,  $F$ , in statistical physics.

**[4 marks]**

- (b) (i) A quantum simple harmonic oscillator has energy levels  $E_n = (n + \frac{1}{2}) \hbar\omega$ . Show that its partition function is given by

$$Z = \frac{e^{-\beta \hbar\omega/2}}{1 - e^{-\beta \hbar\omega}}$$

where  $\beta = \frac{1}{k_B T}$ .

Hence or otherwise show that the average energy of the system is

$$\langle E \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta \hbar\omega} - 1}$$

**[8 marks]**

- (c) (i) State the principle of equipartition of energy.

**[2 marks]**

- (ii) For dilute hydrogen bromide gas (HBr) the characteristic temperatures associated with the rotational and vibrational degrees of freedom are

$$T_{rot} = \frac{\hbar^2}{2 I k_B} \sim 12.1 K \text{ and } T_{vib} = \frac{\hbar\omega}{k_B} \sim 3000 K.$$

Calculate its heat capacity,  $C_V$ , at  $1000 K$ , stating the contributions of the translational, rotational and vibrational degrees of freedom. In each case give a justification for your answer.

**[6 marks]**

3.

(a)

- (i) State the first law of thermodynamics. If you use an equation then define all terms used.

**[2 marks]**

- (ii) From the differential expression for entropy

$$dS = \frac{dU + p dV}{T}$$

show that

$$\left. \frac{\partial S}{\partial U} \right|_V = \frac{1}{T}$$

**[2 marks]**

- (iii) The probability,  $p$ , that a system occupies a state with energy  $U$  can be written as

$$p \propto e^{S/k_B}$$

By making a Taylor expansion of the entropy and inserting it into this expression show that the fluctuations in the energy obey

$$\langle \Delta U^2 \rangle = k_B T^2 C_V$$

where  $C_V = \left. \frac{\partial U}{\partial T} \right|_V$  is the heat capacity at constant volume.

[Note: Normal distribution with standard deviation  $\sigma$  and mean  $\mu$  is given by

$$p(x) \propto e^{-(x-\mu)^2/(2\sigma^2)}]$$

**[6 marks]**

- (b) (i) Give an equation for the grand partition function  $\Xi$ , defining all the symbols used.

**[2 marks]**

- (ii) Show, for a reservoir of Fermi particles in contact with single quantum state of energy  $\epsilon$ , that the average number of Fermi particles in this state is given by the Fermi-Dirac distribution

$$\langle n \rangle = \frac{1}{1 + e^{(\epsilon - \mu)/(k_B T)}}$$

**[6 marks]**

- (iv) Sketch the Fermi-Dirac distribution, and comment on its limits at high and low temperatures.

**[2 marks]**

Internal Examiner: Dr J M Adams  
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