### **FORMULA SHEET**

# **Boltzmann Entropy**

 $S = k \ln W$ 

## **Statistics and Distributions**

Boltzmann	$W_B = N! \prod_{j=1}^n \frac{g_j^{N_j}}{N_j!}$	$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT}$	$Z = \sum_{j=1}^{n} g_j e^{-\varepsilon_j/kT}$
Maxwell-Boltzmann	$W_{MB} = \prod_{j=1}^{n} \frac{g_j^{N_j}}{N_j!}$	$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT}$	$Z = \sum_{j=1}^{n} g_j e^{-\varepsilon_j/kT}$
Fermi-Dirac	$W_{FD} = \prod_{j=1}^{n} \frac{g_j!}{N_j! (g_j - N_j)!}$	<u>)</u> !	$\frac{N_j}{g_j} = \frac{1}{e^{(\varepsilon_j - \mu)/kT} + 1}$
Bose-Einstein	$W_{BE} = \prod_{j=1}^{n} \frac{(N_j + g_j - 1)}{N_j! (g_j - 1)!}$	<u>!</u>	$\frac{N_j}{g_j} = \frac{1}{e^{(\varepsilon_j - \mu)/kT} - 1}$

# **Thermodynamic Potentials**

Internal energy	U	dU = TdS - PdV
Enthalpy	H = U + PV	dH = TdS + VdP
Helmholtz function	F = U - TS	dF = -SdT - PdV
Gibbs function	G = U - TS + PV	dG = -SdT + VdP

## **Statistical Mechanics** Canonical

Internal energy 
$$U = NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V$$
 Pressure  $P = NkT \left(\frac{\partial \ln Z}{\partial V}\right)_T$ 

## Mathematical identities

$\ln N! \approx N \ln N - N$	$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$	$\frac{x}{5} = 1 - e^{-x} \implies x = 4.96$
$1 + y + y^2 + \dots = \frac{1}{1 - y}$	$\int_{-\infty}^{\infty} dx e^{-x^2/\alpha} = \sqrt{\pi\alpha}$	$\int_{-\infty}^{\infty} d\varepsilon \varepsilon^{1/2} e^{-\varepsilon/\alpha} = \frac{\alpha}{2} \sqrt{\pi\alpha}$

#### **QUESTION 1** (20 marks)

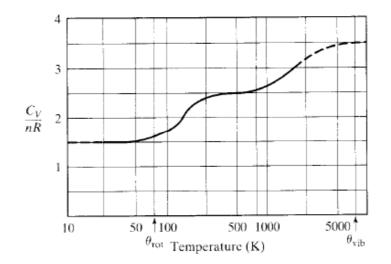
(a) A system of four distinguishable particles has allowed energy levels  $0,\varepsilon,2\varepsilon,3\varepsilon,...$ , and has a total energy  $U = 6\varepsilon$ . Tabulate the nine possible distributions of the four particles among the allowed energy levels. Calculate the thermodynamic weight of each macrostate and the average occupation number of each of the energy levels  $0,\varepsilon,2\varepsilon,3\varepsilon,4\varepsilon,5\varepsilon,6\varepsilon$ .

(b) Tabulate the possible distributions if the particles are indistinguishable.

(c) Tabulate the possible distributions if the particles are fermions and the energy levels are nondegenerate.

### **QUESTION 2** (20 marks)

The figure below shows the experimental values of the heat capacity  $C_v/nR$  for hydrogen.



(a) Explain the qualitative behaviour of the heat capacity from both the classical and quantum approach. In particular, what features can be explained or predicted in each approach.

(b) If the diatomic molecules are considered to be oscillators with energy levels  $\varepsilon_i = (j + \frac{1}{2})hv$ , derive the partition function and the energy.

## **QUESTION 3** (20 marks)

(a) For the classical partition function

$$Z(\beta) = \int dq dp \exp[-\beta H(q, p)]$$

show that the average energy

$$U = \frac{1}{Z} \int dq dp H \exp[-\beta H]$$

can be written in terms of a derivative of the partition function (with respect to  $\beta$ ).

(b) The heat capacity at constant volume is equal to

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

Express  $C_V$  as a derivative of  $\ln Z$ .

(c) For an ideal gas where the Hamiltonian function is

$$H(q,p) = \frac{1}{2m} \sum_{i} \left( p_{xi}^2 + p_{yi}^2 + p_{zi}^2 \right),$$

calculate the partition function.

(d) Hence show the pressure of the ideal gas is

$$P = \frac{NkT}{V}$$

## **QUESTION 4** (20 marks)

(a) Derive the chemical potential for a system of fermions at T = 0 when the density of states is given by

$$g(\varepsilon)d\varepsilon = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \varepsilon^{1/2} d\varepsilon.$$

(b) Verify that the average energy per fermion is  $\frac{3}{5}\varepsilon_F$  at absolute zero by making a direct calculation of U(0)/N.

(c) Similarly, prove that the average speed of a fermion gas particle at T = 0 is  $\frac{3}{4}v_F$ , where the Fermi velocity  $v_F$  is defined by  $\varepsilon_F = \frac{1}{2}mv_F^2$ .

#### **QUESTION 5** (20 marks)

(a) A Bose gas at low temperature ( $T < T_B$ , where  $T_B$  is the Bose temperature) has an internal energy of

$$U = 0.77 NkT \left(\frac{T}{T_B}\right)^{3/2}$$

determine the heat capacity at constant volume.

(b) As the result for the heat capacity is correct at zero temperature, we can calculate the entropy by integrating the heat capacity

$$S = \int_0^T \frac{C_V}{T'} dT'.$$

(c) Thus show that the Helmholtz function is given by

$$F = -0.51NkT \left(\frac{T}{T_B}\right)^{3/2}$$

(d) In the Bose temperature is given by

$$T_B = \frac{h^2}{2\pi mk} \left(\frac{N}{2.612V}\right)^{2/3}$$

use the Helmholtz function to find the pressure.

(e) Show that this system satisfies the ideal gas relation

$$P = \frac{2U}{3V}.$$

(f) If the expression for the maximum wavelength of blackbody radiation is  $\lambda_{\max}T = 2.9 \times 10^{-3} \text{ m K}$ , what is the lowest temperature for which the maximum is in the visible region  $400 \times 10^{-9} < \lambda < 750 \times 10^{-9}$ ? With increasing temperature which end of the spectrum appears first?