## THE UNIVERSITY OF NEW SOUTH WALES

SCHOOL OF PHYSICS FINAL EXAMINATION JUNE 2008

#### **PHYS3020**

# **Statistical Physics**

Time Allowed – 2 hours Total number of questions - 5 Answer ALL questions All questions ARE of equal value Candidates may not bring their own calculators. The following materials will be provided by the Enrolment and Assessment Section: Calculators. Answers must be written in ink. Except where they are expressly required, pencils may only be used for drawing, sketching or graphical work

### FORMULA SHEET

**Boltzmann Entropy**  $S = k \ln W$ 

**Statistics and Distributions** 

Boltzmann 
$$W_{B} = N! \prod_{j=1}^{n} \frac{g_{j}^{N_{j}}}{N_{j}!} \qquad \frac{N_{j}}{g_{j}} = \frac{N}{Z} e^{-\varepsilon_{j}/kT} \qquad Z = \sum_{j=1}^{n} g_{j} e^{-\varepsilon_{j}/kT}$$
Maxwell-Boltzmann 
$$W_{MB} = \prod_{j=1}^{n} \frac{g_{j}^{N_{j}}}{N_{j}!} \qquad \frac{N_{j}}{g_{j}} = \frac{N}{Z} e^{-\varepsilon_{j}/kT} \qquad Z = \sum_{j=1}^{n} g_{j} e^{-\varepsilon_{j}/kT}$$
Fermi-Dirac 
$$W_{FD} = \prod_{j=1}^{n} \frac{g_{j}!}{N_{j}!(g_{j} - N_{j})!} \qquad \frac{N_{j}}{g_{j}} = \frac{1}{e^{(\varepsilon_{j} - \mu)/kT} + 1}$$
Bose-Einstein 
$$W_{BE} = \prod_{j=1}^{n} \frac{(N_{j} + g_{j} - 1)!}{N_{j}!(g_{j} - 1)!} \qquad \frac{N_{j}}{g_{j}} = \frac{1}{e^{(\varepsilon_{j} - \mu)/kT} - 1}$$
Microcanonical 
$$f_{mc}(q, p) = \frac{\delta(H(q, p) - E)}{\int dq dp \delta(H(q, p) - E)}$$
Canonical 
$$f_{C}(q, p) = \frac{\exp(-\beta H(q, p))}{Z(N, V, T)} \qquad Z(N, V, T) = \int dq dp \exp(-\beta H(q, p))$$
Grand-canonical 
$$f_{G}(q, p) = \frac{\exp(\beta(\mu N - H))}{\Xi(\mu, V, T)} \qquad \Xi(\mu, V, T) = \sum_{N=0}^{\infty} z^{N} Z(N, V, T)$$
Thermodynamic Potentials
Internal energy 
$$U \qquad dU = TdS - PdV$$

65	-	
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 Ensemble

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

## Mathematical identities

$\ln N! \approx N \ln N - N$	$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$	$\frac{x}{5} = 1 - e^{-x} \implies x = 4.96$
$1 + y + y^2 + \dots = \frac{1}{1 - y}$	$\int_{-\infty}^{\infty} dx e^{-x^2/\alpha} = \sqrt{\pi\alpha}$	$\int_0^\infty d\varepsilon \varepsilon^{1/2} e^{-\varepsilon/\alpha} = \frac{\alpha}{2} \sqrt{\pi\alpha}$
$\sinh(x) = \frac{e^x - e^{-x}}{2}$	$\frac{d}{dx}\sinh(x) = \cosh(x)$	$\operatorname{csch}(x) = \frac{1}{\sinh(x)}$
$\cosh(x) = \frac{e^x + e^{-x}}{2}$	$\frac{d}{dx}\cosh(x) = \sinh(x)$	$\operatorname{sech}(x) = \frac{1}{\cosh(x)}$
$\tanh(x) = \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}}$	$tanh(x) = \frac{\sinh(x)}{\cosh(x)}$	$\frac{d}{dx}\tanh(x) = \operatorname{sech}^2(x)$
$\operatorname{coth}(x) = \frac{e^{x} + e^{-x}}{e^{x} - e^{-x}}$	$\operatorname{coth}(x) = \frac{\cosh(x)}{\sinh(x)}$	$\frac{d}{dx} \coth(x) = -\operatorname{csch}^2(x)$

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

(a) A system of four distinguishable particles has allowed nondegenerate energy levels  $0,\varepsilon,2\varepsilon,3\varepsilon,...$ , and has a total energy  $U = 7\varepsilon$ . Tabulate all possible distributions of the particles among the allowed energy levels. Calculate the thermodynamic weight of each macrostate and the average occupation number of each of the energy levels  $0,\varepsilon,2\varepsilon,3\varepsilon,...$ 

(b) Tabulate the possible distributions if the particles are indistinguishable bosons and calculate the average occupation number of each level.

(c) Tabulate the possible distributions if the particles are fermions and the energy levels are nondegenerate and calculate the average occupation number of each level.

(d) In part (a), if energy level  $3\varepsilon$  is missing, what is the average occupation of energy level  $7\varepsilon$ ?

The partition function for a system with energy levels  $\varepsilon_j$ , with degeneracies  $g_j$ , is given by

$$Z = \sum_{j=1}^{n} g_j e^{-\varepsilon_j/kT}$$

(e) If the density of states function  $g(\varepsilon)d\varepsilon = (4\sqrt{2}\pi V/h^3)m^{3/2}\varepsilon^{1/2}d\varepsilon$ , approximate the sum in the partition function by an integral and derive the result

$$Z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

(f) Calculate the internal energy and pressure for this system.

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





(a) Explain the qualitative behaviour of the heat capacity from both the classical and quantum approach. What are the deficiencies of the classical approach? How does the quantum mechanical approach remedy these deficiencies? Note that  $\theta_{rot} = \hbar^2/2Ik$  and  $\theta_{vib} = hv/k$ .

(b) If the diatomic molecules are considered to be oscillators with energy levels  $\varepsilon_i = (j + \frac{1}{2})hv$ , show that the partition function is given by

$$Z = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}}$$

(c) Derive the energy and the heat capacity for this system of oscillators.

(d) Discuss the behaviour of the heat capacity as  $T \rightarrow 0$  and as  $T \rightarrow \infty$ .

(e) Explain how the graph of the experimental heat capacity would change if hydrogen is replaced by deuterium.

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

(a) For a classical system of N particles with Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \Phi(\mathbf{q}_1, \dots, \mathbf{q}_N)$$

show that the canonical partition function is given by

$$Z = \int d\mathbf{p}_1 \dots d\mathbf{p}_N \int d\mathbf{q}_1 \dots d\mathbf{q}_N \exp(-\beta H) = \left(2\pi m kT\right)^{3N/2} \int d\mathbf{q}_1 \dots d\mathbf{q}_N \exp(-\beta \Phi)$$

(b) For an ideal gas the potential is equal to zero everywhere (except at collisions). Write down the ideal gas canonical partition function.

(c) Use the canonical partition function to calculate the average internal energy and pressure of an ideal gas.

(d) If the classical average of an arbitrary phase variable X is given by

$$\left\langle X\right\rangle = \frac{\int dq dp X e^{-\beta H}}{\int dq dp e^{-\beta H}},$$

show that

$$\frac{\partial}{\partial \beta} \ln Z = -U$$

and

$$\frac{\partial^2}{\partial \beta^2} \ln Z = \left\langle U^2 \right\rangle - \left\langle U \right\rangle^2.$$

(e) Show that the mean square fluctuation in the internal energy  $\langle \Delta U^2 \rangle = \langle U^2 \rangle - \langle U \rangle^2$  in the canonical ensemble is determined by the heat capacity at constant volume.

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

(a) Photons in a cavity obey Bose-Einstein statistics. If the number of quantum states with frequencies in the range v to v + dv is

$$g(v)dv = \frac{8\pi V}{c^3}v^2dv$$

show that the energy density is

$$u(v)dv = \frac{8\pi hV}{c^3} \left(\frac{v^3 dv}{e^{hv/kT} - 1}\right)$$

(b) Find the total energy density (energy per unit volume) by integrating over wavelength  $(\lambda = c/v)$ . If the total energy density can be written as

$$\frac{U}{V} = aT^4$$

find the explicit expression for the constant a.

(c) Explain how the energy density as a function of wavelength given above (Planck's law) is related to the Rayleigh-Jeans law  $u(\lambda)d\lambda \approx 8\pi kTVd\lambda/\lambda^4$ , and to Wien's law

$$u(\lambda)d\lambda \approx V\left(\frac{8\pi hc}{\lambda^5}\right)e^{-hc/\lambda kT}d\lambda.$$

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

(a) For a system of fermions where the density of states is given by

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

Show that the Fermi energy at T = 0 is given by

$$\mu(0) = \frac{h^2}{2m} \left(\frac{3N}{8\pi V}\right)^{2/3}$$

(b) The internal energy of a fermion gas is

$$U = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT} + 1}$$

Explain the interplay between the numerator and denominator of the integrand in determining the value of the internal energy.

(c) The electronic contribution to the internal energy is

$$U \approx \frac{3}{5} N \varepsilon_F \left( 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 - \ldots \right)$$

Find an expression for the electronic heat capacity.

(d) The internal energy can be written as an infinite sum with a set of undetermined coefficients

$$U = \frac{3}{5} N k T_F \sum_{i=0}^{\infty} a_i \left(\frac{T}{T_F}\right)^{2i},$$

where

$$T_F = \frac{h^2}{2mk} \left(\frac{3N}{8\pi V}\right)^{2/3}.$$

The dependence on T is explicit and  $T_F$  is a function of V. Show that the entropy is given by

$$S = \int_{0}^{T} \frac{1}{T'} \frac{\partial U}{\partial T'} dT' = \frac{3}{5} NkT_{F} \sum_{i=1}^{\infty} \frac{2i}{2i-1} a_{i} \left( \frac{T^{2i-1}}{T_{F}^{2i}} \right).$$

Show that the Helmholtz function is

$$F = U - TS = \frac{3}{5}NkT_F \left\{ 1 - \sum_{i=1}^{\infty} \frac{a_i}{2i - 1} \left(\frac{T}{T_F}\right)^{2i} \right\}.$$

Hence, or otherwise, show that the relation  $P = \frac{2}{3}(U/V)$  is exact for the fermion gas.