FORMULA SHEET

Boltzmann Entropy

$$S = k \ln W$$

Statistics and Distributions

Boltzmann $\quad W = N! \prod_{j=1}^{n} \frac{g_j^{N_j}}{N_j!} \quad \frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT} \quad Z = \sum_{j=1}^{n} g_j e^{-\varepsilon_j/kT}$

Maxwell-Boltzmann $\quad W = \prod_{j=1}^{n} \frac{g_j^{N_j}}{N_j!} \quad \frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT} \quad Z = \sum_{j=1}^{n} g_j e^{-\varepsilon_j/kT}$

Fermi-Dirac $\quad W = \prod_{j=1}^{n} \frac{g_j!}{N_j!\left(g_j - N_j\right)!} \quad \frac{N_j}{g_j} = \frac{1}{e^{(\varepsilon_j - \mu)/kT} + 1}$

Bose-Einstein $\quad W = \prod_{j=1}^{n} \frac{(N_j + g_j - 1)!}{N_j!\left(g_j - 1\right)!} \quad \frac{N_j}{g_j} = \frac{1}{e^{(\varepsilon_j - \mu)/kT} - 1}$

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	$G = U - TS + PV$	$dG = -SdT + VdP$

Mathematical identities

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15} \qquad \frac{x}{5} = 1 - e^{-x} \quad \Rightarrow \quad x = 4.96$$

QUESTION 1 (20 marks)

(a) For the classical partition function

$$Z = \int dq dp \exp[-\beta H]$$

show that the average energy $\langle U \rangle = (1/Z)\int dq dp H \exp[-\beta H]$ can be written in terms of a derivative of the partition function with respect to β.

(b) Fluctuations in energy can be measured by considering the difference between the instantaneous energy and its average value $\Delta U = U - \langle U \rangle$. The average of this quantity is zero, but the average of its square is not zero. Show that

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

(c) What happens to the relative fluctuations

$$\frac{\sqrt{\langle U^2 \rangle - \langle U \rangle^2}}{\langle U \rangle}$$

as the system becomes large ($N \to \infty$).

QUESTION 2 (20 marks)

(a) Derive the classical equipartition theorem for the canonical distribution. That is, show that each "degree of freedom" contributes $\frac{1}{2}kT$ to the internal energy of the system.

(b) Explain the application of the equipartition theorem to monatomic gases, diatomic gases and harmonic solids, indicating the "degrees of freedom" in each case.

(c) What quantum concepts are required to explain the steps in the heat capacity of a diatomic gas? What parameters effect the position of the steps for different gases?

QUESTION 3 (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) For a system of noninteracting electrons, show that the probability $f(\varepsilon)$ of finding an electron in a state with energy Δ above the chemical potential μ is the same as the probability of finding an electron absent from a state with energy Δ below μ at any given temperature.

QUESTION 4 (20 marks)

(a) Use Boltzmann statistics to calculate the partition function

$$Z = \left(\frac{e^{-\theta_E/2T}}{1-e^{-\theta_E/T}}\right),$$

the Helmholtz function F, the internal energy U and the heat capacity of the quantum harmonic oscillator with energy levels $\varepsilon_j = (j+\frac{1}{2})h\nu, \quad j = 0,1,2,..$

(b) Use the results to calculate the lattice heat capacity of a crystalline solid in the Einstein model. Consider the low-temperature and high-temperature limits and explain the results. Plot the graph of $C_V(T)$.

QUESTION 5 (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

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

show that the energy density is

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

(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) Find the wavelength for which the $u(\lambda)$ is a maximum.