1.

(a) State the first law of thermodynamics, and give a corresponding equation defining all the symbols used.

[2 marks]

(b) For a polymer of length l under tension f the change in entropy can be expressed as

$$dS = \frac{dU - f\ dl}{T}$$

(i) In this equation state what the term $f\ dl$ represents.

[2 marks]

(ii) Show that the tension, f, in the polymer can be expressed as

$$f = -T \frac{\partial S}{\partial l}\Big|_U$$

[4 marks]

(c) A simple $1D$ model of a polymer consists of N connected monomers that step either to the left or to the right.

(i) If $N - m$ of these links point to the right and $N + m$ point to the left, show that the Boltzmann entropy can be expressed as

$$S = k_B[N \ln N - (N + m)\ln(N + m) - (N - m)\ln(N - m)]$$

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

[3 marks]

(ii) Hence show, using the differential expression in (b) (ii) and then using the chain rule, that the tension in the rubber is given by

$$f = \frac{k_B\ T\ l}{2\ N\ a^2}$$

where $l = 2\ m\ a$ is the length of the polymer.

[Note: $\ln \frac{N+m}{N-m} \approx \frac{2\ m}{N}$ for $m \ll N$]

[7 marks]

(iii) A polymer at fixed tension contracts as the temperature is raised. Give a microscopic explanation of the behaviour of crystalline materials under the same conditions.

[2 marks]

2.

(a) A parallel plate capacitor has a plate area of $1\ \mu m^2$ and a plate spacing of $100\ nm$. At what temperature will the thermal energy be enough to excite a charge of one electron?

[8 marks]

(b) (i) Write down a general expression for the partition function Z and define all symbols used.

[2 marks]

(ii) A simple harmonic oscillator has energy levels given by

$$\epsilon = n\hbar\omega$$

where n is an integer from 0 to ∞, and ω is the oscillation frequency. Show that its partition function is

$$Z = \frac{1}{1-e^{-\hbar\omega/(k_B T)}}.$$

[4 marks]

(iii) The carbon monoxide molecule has a bond vibration frequency of $4 \times 10^{14}\ s^{-1}$ and a moment of inertia of $4.5 \times 10^{-40}\ kg\ m^2$.

Calculate the temperature above which the vibrational degrees of freedom of carbon monoxide reach their equipartition value of average energy.

[2 marks]

(iv) Calculate the temperature above which the rotational degrees of freedom of carbon monoxide reach their equipartition value of average energy.

[2 marks]

(v) Sketch the temperature dependence of the heat capacity of carbon monoxide.

[2 marks]