

# Homework 4

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**4.1** (a) One kilogram of water at  $0^\circ\text{C}$  is brought into contact with a large heat reservoir at  $100^\circ\text{C}$ . When the water has reached  $100^\circ\text{C}$ , what has been the change in entropy of the water? of the heat reservoir? of the entire system consisting of both the water and heat reservoir?

(b) If the water had been heated from  $0^\circ\text{C}$  to  $100^\circ\text{C}$  by first bringing it in contact with a reservoir at  $50^\circ\text{C}$  and then with a reservoir at  $100^\circ\text{C}$ , what would have been the change of entropy of the entire system?

(c) Show how the water might be heated from  $0^\circ\text{C}$  to  $100^\circ\text{C}$  with no change in the entropy of the entire system.

**4.2** A 750-g copper calorimeter containing 200 g of water is in equilibrium at a temperature of  $20^\circ\text{C}$ . An experimenter now places 30 g of ice at  $0^\circ\text{C}$  in the calorimeter and encloses the latter with a heat-insulating shield.

(a) When all the ice has melted and equilibrium has been reached, what will be the temperature of the water? (The specific heat of copper is  $0.418\text{ J/g}\cdot\text{K}$ . Ice has a specific gravity of 0.917 and its heat of fusion is  $333\text{ J/g}$ ; i.e. it requires  $333\text{ J}$  of heat to convert  $1\text{ g}$  of ice to water at  $0^\circ\text{C}$ .)

(b) Compute the total entropy change resulting from the process of part (a).

(c) After all the ice has melted and equilibrium has been reached, how much work, in joules, must be supplied to the system (e.g. by means of a stirring rod) to restore all the water to  $20^\circ\text{C}$ ?

**4.3** The heat absorbed by a mole of ideal gas in a quasi-static process in which its temperature  $T$  changes by  $dT$  and its volume  $V$  by  $dV$  is given by  $dQ = c dT + \bar{p} dV$  where  $c$  is its constant molar specific heat at constant volume and  $\bar{p}$  is its mean pressure,  $\bar{p} = RT/V$ . Find an expression for the change of entropy of this gas in a quasi-static process which takes it from initial values of temperature  $T_i$  and volume  $V_i$  to the final values  $T_f$  and  $V_f$ . Does your answer depend on the process involved in going from the initial to the final state?

**4.4** A solid contains  $N$  magnetic atoms having spin  $\frac{1}{2}$ . At sufficiently high temperatures, each spin is completely randomly oriented, i.e., equally likely to be in either of its two possible states. But at sufficiently low temperatures the interactions between the magnetic atoms causes them to exhibit ferromagnetism, with the result that all their spins become oriented along the same direction as  $T \rightarrow 0$ . A very crude approximation suggests that the spin-dependent contribution  $C(T)$  to the heat capacity of this solid has an approximate temperature dependence given by

$$C(T) = \left\{ \begin{array}{ll} C_1(2\frac{T}{T_1} - 1) & \text{if } \frac{1}{2}T_1 < T < T_1 \\ 0 & \text{otherwise} \end{array} \right\}$$

The abrupt increase in specific heat as  $T$  is reduced below  $T_1$  is due to the onset of ferromagnetic behavior. Use entropy considerations to find an explicit expression for the maximum value  $C_1$  of the heat capacity.

**5.** A very simple model of a polymer of length  $L$  treats it as a 1-dimensional random walk that has  $N$  steps, where each step has length  $b = \frac{L}{N}$ . This step length is called the Kuhn length. Suppose one end of this polymer is at the origin and the other is at  $x$ .

(a) Solve for  $\Omega(n_1)$ , where there are  $n_1$  steps to the right and  $n_2 = N - n_1$  steps to the left.

(b) Solve for  $\Omega(x)$ , expressing the result only in terms of  $L$ ,  $b$ , and  $x$ .

- (c) Compute  $\ln \Omega(x)$  using Stirling's approximation.
- (d) Compute the mean polymer tension,  $\bar{F}$ ; this is the generalized force that corresponds to parameter  $x$ .
- (e) Compute the Hooke's law spring constant for the polymer for small displacements, in which  $x \ll L$ .
- 6.** The density of states for an ideal monatomic gas is  $\Omega(V, E) = BV^N E^{3N/2}$ . Using this, compute
- (a) the molar heat capacity at constant volume and
- (b) the molar heat capacity at constant pressure.
- 7.** The density of states for  $N$  classical harmonic oscillators is  $\Omega(E) = (\frac{E}{\hbar\omega})^N$ . Compute the
- (a) entropy and
- (b) molar heat capacity for these classical harmonic oscillators.
- 8.** The energy of a quantum harmonic oscillator of frequency  $\omega$  can be  $\frac{1}{2}\hbar\omega, \frac{3}{2}\hbar\omega, \frac{5}{2}\hbar\omega$  etc. Consider a system containing  $N$  independent harmonic oscillators which has total energy  $E = \frac{1}{2}N\hbar\omega + M\hbar\omega$ , where  $N$  and  $M$  are integers.
- (a) Find the density of states for this system (this will be covered in class).
- (b) Compute the entropy for this system.
- (c) Compute the molar heat capacity.
- (d) Graph your answer and compare the result to that of the previous problem.