Statistical Mechanics and Thermodynamics
August 2015

You may refer to a statistical mechanics text of your choice, but no other notes or references.

Answer one of the following two problems.

1. The dihydrogen molecule can exist in either of two states: parahydrogen in which the nuclear spins are antiparallel giving the molecule a ground-state total spin angular momentum of zero; and orthohydrogen in which the nuclear spins are aligned giving the molecule a total spin angular momentum of 1 hbar and z-projections of spin $s_z = +1\hbar$, 0, or $-1\hbar$. The transition between the two forms occurs very slowly in the absence of a catalyst.

   (a) An insulated, rigid box of volume $2V$ is prepared with n moles of dilute parahydrogen gas held in one half of the box by a partition. The pressure is P and the temperature is T. The partition is suddenly removed and the gas fills the entire box. After equilibrium is reached, (i) What is the new pressure? (ii) What is the new temperature? (iii) How much heat Q was added to or removed from the gas? (iv) What is the change in entropy?

   (b) An insulated, rigid box of volume $2V$ is prepared with n moles of dilute parahydrogen gas held in each half of the box by a partition. The pressure is P and the temperature is T. The partition is suddenly removed and the gas mixes in the entire box. After equilibrium is reached, what is the change in entropy?

   (c) An insulated, rigid box of volume $2V$ is prepared with n moles of dilute parahydrogen gas held in one half of the box by a partition. The other half of the box contains n moles of orthohydrogen. The pressure is P and the temperature is T. The partition is suddenly removed and the gas mixes in the entire box. After equilibrium is reached, what is the change in entropy?

   (d) Explain why changes in entropy may be calculated even if the system is not moving through equilibrium states.

   (e) At room temperature, where $k_B T$ is far above the energy difference between para- and orthohydrogen, and if you wait long enough for transitions to occur, what is the equilibrium ratio of the two forms of hydrogen.

2. Give all answers in scientific notation to two significant figures.

   Given 100 distinguishable coins which can show either heads or tails,

   (a) How many possible states N_s are there?

   (b) How many states have no heads showing?

   (c) How many states have exactly one head showing?

   (d) How many states have exactly two heads showing?

   (e) If the coins are randomized, what is the most likely number of heads showing?

   (f) How many states have this most likely number of heads showing?

   (g) What fraction of the total number of states is this?

   (h) If another 100 coins are added to the original 100, what is the new number of possible states in terms of the original number N_s?

   (i) Is the number of possible states extrinsic? If yes, explain why; if no, suggest an extrinsic quantity.

Answer one of the following two problems.

3. A gas satisfies the relation

$$E = \frac{aS^4}{NV^2}$$

where a is a constant and N are the number of particles, which are held fixed here. This gas is run through the thermodynamic cycle pictured.

Here AB is an isotherm (constant T), AC is adiabatic (no heat Q absorbed), and BC is an isochore (constant V). The volume ratio $V_C/V_A = 2$.

(a) State the thermodynamic relationship relating differential changes in energy, entropy and volume. (Don't derive, just quote.)

(b) You may choose to consider either S, V or E, V as your two independent variables. Derive an expression for temperature T and pressure P in terms of your independent variables.

(c) Use your results to derive an equation of state for this system. (That is, an equation relating the easily measurable quantites V, T, P and N.)

(d) Compute the ratio P_B/P_A.

(e) Compute the ratio P_C/P_A.

(f) Find an expression for the work done by the system during AB for fixed temperature T.

4. The figure illustrates a soap film (shown in gray) supported by a wire frame. Because of surface tension the film exerts a force $2\sigma\ell$ on the cross wire. This force is in such a direction that it tends to move this wire so as to decrease the area of the film. The quantity σ is called the surface tension of the film, and the factor 2 occurs because the film has two surfaces. The temperature dependence of σ is given by

$$\sigma = \sigma_0 - \alpha T \tag{1}$$

where σ_0 and α are constants independent of T or x.

(a) Suppose that the distance x is the only external parameter of significance in the problem. Write a relation expressing the change dE in mean energy of the film in terms of the heat dQ absorbed by it and the work done by it in an infinitesimal quasi-static process in which the distance x is changed by an amount dx.

(b) Calculate the change in entropy $\Delta S = S(x) - S(0)$ and the change in mean energy $\Delta E = E(x) - E(0)$ of the film when it is stretched at a constant temperature T_0 from a length $x = 0$ to a length x.

(c) Calculate the work $W(0 \to x)$ done and heat $Q(0 \to x)$ absorbed by the film as it is stretched at this constant temperature from a length $x = 0$ to a length x.

Answer one of the following two problems.

5. A classical ideal gas of N indistinguishable monatomic particles is in a cylindrical vessel of cross section A. The top of the vessel is closed by a freely movable piston of mass M. The system is in thermal contact with a reservoir at temperature T. You may neglect the gravitational potential for the gas molecules.

   (a) Calculate the partition function for the system consisting of gas plus piston

   (b) Determine the average volume, the equation of state, and the heat capacity.

   (c) Discuss which heat capacity you are calculating.

6. Consider a three-state paramagnet in which an atom with a total spin of $1\hbar$ can have a z-projection of spin of $+1\hbar$, 0, or $-1\hbar$. The corresponding energies are $+\mu B$, 0, and $-\mu B$. There are a total of N atoms. μB is a few electron volts. The system is in thermal contact with a reservoir at temperature T.

   (a) What is the partition function of the system?

   (b) At an absolute temperature of a few nanokelvin, what are the occupancies of the three states?

   (c) At an absolute temperature of a few gigakelvin, what are the occupancies of the three states?

   (d) If the system is in thermal contact with a reservoir with $k_B T = \mu B/2$, what are the occupancies of the three states?

   (e) What is the Helmholtz free energy of the system?

   (f) What is the average energy of the system?

   (g) What is the magnetic moment of the system as a function of temperature?