Assignment 6

These problems are from Pathria, but I've reworded them to be (I hope) a little clearer.

6.1 (Pathria 3.14.) (a) Consider an ideal-gas mixture of atoms A, atoms B, and molecules AB. The particle undergo the reaction $AB \leftrightarrow A + B$. If ρ_A, ρ_B, and ρ_{AB} are the respective densities, show that in equilibrium,

$$\frac{\rho_{AB}}{\rho_A \rho_B} = V \frac{Q_{AB}}{Q_A Q_B} = K(T),$$

where V is the volume of the system and the Q_i are the single-particle partition functions. This relation is known as the law of mass action, and $K(T)$ is referred to as the equilibrium constant. *Hint*: If the volume of the system is fixed, the Helmholtz free energy will be minimized at equilibrium.

(b) Find the analogous relation for the reaction $2A + B \leftrightarrow A_2B$.

6.2 (Pathria 3.15) Consider again an extreme relativistic ideal gas consisting of N monatomic particles with energy-momentum relationship $\epsilon = pc$. Show that the partition function $Q_N(V,T)$ is given by

$$Q_N(V,T) = \frac{1}{N!} \left\{ 8\pi V \left(\frac{kT}{hc} \right)^3 \right\}^N .$$

Calculate the entropy from this, and verify that it is the same obtained in problem 5.2. (Note that this calculation should be much easier than last week's.)

6.3 (Pathria 3.24) Show that for a relativistic (but not extreme relativistic) ideal gas, the equipartition theorem takes the form

$$\left\langle m_0 u^2 \left(1 - u^2/c^2\right)^{-1/2} \right\rangle = 3k_B T,$$

where m_0 is the rest mass of a particle and u its speed. (Recall that $\epsilon = \sqrt{p^2c^2 + m^2c^4}$ in general.) Verify that in the extreme relativistic case, the mean thermal energy per particle is twice its value as in the nonrelativistic limit.

6.4 (Pathria 3.29) The potential energy of a one-dimensional *anharmonic* oscillator may be written as

$$V(q) = cq^2 - gq^3 - fq^4,$$

where c, g, and f are positive constants. Assume that g and f are very small. Show that the leading contribution of the anharmonic terms to the heat capacity of the oscillator (assumed classical) is given by

$$\frac{3}{2}k^2 \left(\frac{f}{c^2} + \frac{5}{4}\frac{g^2}{c^3} \right) T$$

and, to the same order, the mean value of the position coordinate q is given by

$$\frac{3}{4}\frac{gkT}{c^2}.$$

Hint: This can be solved by Taylor expanding the expression for the partition function. If you look carefully, the expansion is invalid at large q, but the integrand is anyway very small in that limit.