Phys 971 Stat Mech: Homework 4

due 10/22/2013

1

A surface with N adsorption sites is in equilibrium with a mixed ideal gas containing molecules of type A and B. Each site can take either one single A molecule with energy $-\epsilon_A$ or a single B molecule with energy $-\epsilon_B$. Compute the grand canonical partition function for this adsorbed system. Then find relations between the fractional occupations ($\theta_A = \bar{N}_A/N$ and $\theta_B = \bar{N}_B/N$) and the partial pressures p_A and p_B.

2

Pathria 5.1 Evaluate the density matrix ρ_{mn} of an electron spin in the representation which makes $\hat{\sigma}_x$ diagonal. Next show that the value of $\langle \sigma_z \rangle$, resulting from this representation, is precisely the same as the one obtained in Sec. 5.3. Hint: the representation needed here follows from the one used in Sec. 5.3 by carrying out a transformation with the help of the unitary operator

$$\hat{U} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

3

Pathria 5.3 Derive the density matrix ρ for (i) a free particle, and (ii) a linear harmonic oscillator in the *momentum* representation and study its properties along the lines of Sec. 5.3.

4

Pathria 6.32 Derive an expression for the equilibrium constant $K(T)$ for the reaction $N_2 + O_2 \rightleftharpoons 2NO$ in terms of the ground state energy change $\Delta\epsilon_0 = 2\epsilon_{NO} - \epsilon_{N_2} - \epsilon_{O_2}$ and the vibrational and rotational partition function of the diatomic molecule, using results from Section 6.5. Give predictions for the ranges of temperatures where the rotational modes are classically excited but the vibration models are suppressed and for higher temperatures where both the rotational and vibrational modes are classically excited.