Physics 5524

Statistical Mechanics

Problem Set 6

Due: Friday, Feb. 20

6.1 Pathria, Problem 3.35, Page 88.

6.2 Consider an adsorbent surface having N_0 sites which can each adsorb one molecule. Let $a(T)$ be the partition function for a single molecule adsorbed on a particular site. In what follows ignore any interactions between molecules adsorbed on different sites.

(a) Show that the canonical partition function for N adsorbed molecules on this surface is

$$Q_N = \begin{pmatrix} N_0 \\ N \end{pmatrix} a(T)^N.$$

(b) Show that the *grand* partition function for molecules on this surface is

$$\mathcal{Z} = (1 + za(T))^{N_0}.$$

where z is the fugacity. Determine the grant potential for the surface.

(c) Using the result of (b), find an expression for the *covering fraction* of the surface, $\Theta = N/N_0$, as a function of the fugacity (or equivalently the chemical potential, μ) and the temperature, T.

Now assume that this adsorbent surface is in equilibrium with an ideal monatomic gas. Further assume that each adsorbed atom on a particular site of the surface has a single energy level with energy $-\epsilon$. (ϵ is thus the threshold energy required to liberate an adsorbed atom from the surface.)

(d) Obtain the grant partition function for an ideal monatomic gas and determine the grant potential.

(e) Using the result of (d) obtain an expression for the fugacity of this ideal gas as a function of pressure, P, and temperature T.

(f) By setting the fugacities of the gas and the surface equal to one another, obtain an expression for the covering fraction, Θ, as a function of temperature, T, pressure of the gas, P, and the threshold energy ϵ. Study the high and low pressure limits and verify that your result makes sense in these limits.

(g) How does your answer to (f) change if you model the adsorbed atoms as one-dimensional quantum oscillators with angular frequency ω?

6.3 Pathria, Problem 4.8, Page 103.