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University of Oregon; Spring 2008

Physics 353: Problem Set 4 – modified April 28, 2008

Due date: Wednesday, April 30, **5pm**. Due to the Midterm, no late homework will be accepted. **Reading:** Kittel & Kroemer Chapter 5; Chapter 9.

1, 4 pts. Heme groups revisited. Consider, as in class, a single heme group (as in myoglobin) that can hold zero or one O₂ molecules. The energy with zero O₂ is 0; the energy with one is ε . O₂ in myoglobin is in diffusive equilibrium with oxygen dissolved in the surroundings, which you can treat as an ideal gas of concentration n. Neglect the internal degrees of freedom of O₂ (i.e. imagine $Z_{int} = 1$). Derive an expression for f, the probability that a heme group is occupied by O₂ as a function of τ , P, and P_0 , where P is the oxygen pressure (related to the concentration of oxygen by the ideal gas law) and P_0 is a function of τ , ε and various constants. *Hint:* You should find f = 1/2 at $P = P_0$. Suggestion: Define P_0 to have dimensions of pressure, and make f an explicit function of P and P_0 only.

2, 5 pts. A hydrogen-like atom. Consider a hydrogen-like atom that can exist in 1 of 4 states:

state#1, with 1 electron and energy $-\Delta/2$ state#2, with 0 electrons and energy $-\delta/2$ state#3, with 2 electrons and energy $+\delta/2$ state#4, with 1 electron and energy $+\Delta/2$



In other words, the ground and excited states for 1 bound electron are separated by energy Δ , and ionizing the atom involves energy $\frac{\delta}{2}$. Let's say that the average number of electrons per atom is 1. (For example, if we had a crystal of such atoms, it would have to maintain overall charge neutrality.) Using this condition, determine the chemical potential at temperature τ . (*Hint:* Your final answer will **not** depend on all of the above symbols.)

3, 11 pts. The Langmuir model of adsorption. We'll examine the equilibrium between particles "free" in a gas (or solution) and particles adsorbed on a surface, e.g. airborne pollutants adsorbing onto charcoal filters. Consider the surface as having a number of sites A that the particles might occupy. Our goal will be to figure out the fraction of occupied sites as a function of the particle concentration in the (ideal) gas. Note that we already have an expression for μ for the gas.

(a, 2 pts.) Our first task is to derive an expression for the chemical potential of the surface. If there are A

sites occupied by N particles, the number of ways to arrange this is $\Omega = \frac{A!}{N!(A-N)!}$, which you may

recall from Phys. 352. From this, determine the entropy using Stirling's approximation.

- (b, 2 pts.) From the entropy of the surface, determine the chemical potential, μ , at temperature τ using the definition of μ . Express your answer in terms of the occupied fraction of sites: $f \equiv \frac{N}{4}$.
- (c, 3 pts.) Your result from (b) is the "internal" chemical potential of the surface-bound particles. In addition, they have an "external" chemical potential $\mu_{ext} = \varepsilon$, where ε is the binding energy of the particle to the surface (typically a negative number). Consider the adsorbed particles to be in diffusive and thermal equilibrium with the particles in the (ideal) gas, which are at concentration n. Neglect the internal degrees of freedom (i.e. imagine $Z_{int} = 1$; this isn't important). Derive an expression for f in terms of n and $K(\tau)$, where $K(\tau)$ incorporates all the constants and temperature-dependent factors. $K(\tau)$ is the binding constant. Hints: If you've done things properly, $K(\tau)$ should have dimensions of either concentration or 1/concentration (depending on how you define it), and you should find f = 1/2 at $n = K(\tau)$ or $n = 1/K(\tau)$ (depending on how you define K).
- (d, 4 pts.) This model of adsorption applies to many systems, including the binding of proteins in solution onto cellular membranes. The graph below is from data from the Parthasarathy Lab, relating the bound fraction of "Cholera toxin subunit B" (CTB) at a membrane to its concentration in solution¹. The concentration is given in "chemical" units of nM (10^{-9} moles/liter). I've plotted n/f on the vertical scale vs. n on the horizontal scale. Are the data consistent with a Langmuir adsorption model? If so, what is K? Express K in nM. (Answering this might make it clear why it's useful to plot the data in this form.) What CTB concentration in solution would cause 10% of the membrane sites to be occupied? ... 95%?



4, 11 pts (5,1,3,2). **Biopolymer growth: Kittel & Kroemer 9.4.** Some comments: *General:* What we're examining is polymerization – growth or dissolution of a polymer from individual monomers. One can have two monomers in equilibrium with the "2-mer" state: $1mer + 1mer \rightleftharpoons 2mer$, and

 $1mer + 2mer \longrightarrow 3mer$, ... $1mer + Nmer \longrightarrow (N+1)mer$. These monomers may be, for example,

amino acids that connect to form a protein, or styrene molecules that form polystyrene.

(a) Suggestion: First consider the $1mer + Nmer \rightleftharpoons (N+1)mer$ equilibrium, then $1mer + (N-1)mer \rightleftharpoons Nmer$, etc.

(b) Recall how F and Z are related. Keep track of all the " n_0 's."

(c) "Molecular weight" means mass in a.m.u. One a.m.u. is 1.67×10^{-27} kg.

(d) By "goes in the direction of long molecules" we mean that at equilibrium the concentration of an (N+1)-mer is greater than that of an N-mer, etc. – i.e. the polymer is long.

¹ In other words, CTB can exist in solution or can be membrane-bound, where it interacts with particular membrane sites. We want to know the equilibrium between these configurations. The actual experiment is more complicated than these data imply. What's actually measured is the influence of CTB binding on the behavior of membrane-coated microparticles in an optical trap. From this, I've untangled the occupancy fraction, f, and am just presenting this.