PHYSICS 429: Introduction to Biological Physics

May 8 2008 Problem Set 5 solutions These problems are due on Tuesday May 13.

1. Nelson 7.6 -Effects of hydrogen bonds on water

Consider a box with some liquid water and some waer vapor, held at a fixed temperature by an external heat reservoir. When another water molecule leaves the liquid phase, the free energy increases because of the lost H-bonds. Because the temperature is fixed, this energy must come in as heat from the external reservoir. We want to estmate the total energy needed to separate all the water moleculres, and this is the heat of vaporization. Each of the 3.5 bonds is shared between **two** water molecules. To avoid double counting, we must divide by a factor of two. So we have

Energy needed per kilogram = number of bonds (number of molecules /kg) (energy of bond)
$= \frac{3.5}{2}\frac{N_{\mathrm{mole}}}{0.018kg} \times 9k_BT_r$
$= 1.75(\frac{6.023\times 10^{23}}{0.018}) \times 9(4.1\times 10^{-21})$ J/kg $= 2.1\times 10^6$J/kg The measured value in Appendix B page 571 is 2.3×10^6J/kg which is also equivalent to 2.3×10^9J/m^3

2. Nelson 7.10. I will email my mathematica 6 notebook to you. I find that the upper curve corresponds to a surface charge density of $e/14$ nm^2, which is about 50% dissociated.

3. Nelson 7.17. Counter ion cloud. This is on page 591, additional problems.

a. We can take the potential at infinity to be any convenient constant value, and 0 is convenient. The second condition follows from the Gauss law.

b. Solving the equation for $rV(r)$ gives $rV(r) = Ae^{-r/\lambda_D}$, where we have kept the physically reasonable solution. We deterimine the constant A from the boundary condition on the derivative of V at $r = a$. Note that

$$-\frac{dV}{dr}(r=a) = \frac{A}{a}e^{-a/\lambda_D}\left(\frac{1}{a}+\frac{1}{\lambda_D}\right) = \frac{q}{4\pi\varepsilon a^2};$$

solving for A and substituting it in gives

$$V(r) = \frac{q\lambda_D}{4\pi\varepsilon(\lambda_D+a)}\frac{1}{r}e^{-(r-a)/\lambda_D}.$$

c. The negative charge density ρ_q is given by $\rho_q = -\varepsilon\nabla^2 V$. Then the total charge outside Q_{out} the polymer is

$$Q_{\mathrm{out}} = -\varepsilon\int d^3r\nabla^2 V,$$

where the volume of integration is the region between the two spheres at $r = a$ and the large sphere at $r \to \infty$. Use the divergence theorem to replace the volume integral by a surface integral

$$Q_{\mathrm{out}} = -\varepsilon\int dS\hat{n}\cdot\vec{\nabla}V,$$

where $\hat{n} = \hat{r}$ for the surface at infinity and $\hat{n} = -\hat{r}$ for the surface at $r = a$. Then evaluating gives

$$Q_{\mathrm{out}} = -\varepsilon 4\pi\left[\lim r\to\infty\ (r^2\frac{dV}{dr}) - a^2\frac{dV}{dr}(r=a)\right].$$

Evaluating this using the boundary condition gives

$$Q_{\mathrm{out}} = -\varepsilon 4\pi(-a^2)\frac{-q}{4\pi\varepsilon a^2} = -q.$$

d. We just need to integrate the little bits of work $dW = dqV$ at a distance $r = a$. So

$$W = \int_0^q dqV = \int_0^q \frac{q\lambda_D}{4\pi\varepsilon a(\lambda_D + a)} = \frac{q^2\lambda_D}{8\pi\varepsilon a(\lambda_D + a)}.$$

e. As the Debye screening length goes to 0 due to increased ionic strength, the potential energy found in part (c) also vanishes. Increased ionic strength better shields the chared polymer, reducing the free energy cost to insert it into solution and therefore increasing solubility.

4. This is Hobbie-Roth 9.10. A collection of molecular electric dipoles of dipole moment vector $\mathbf{p}$ are in thermal equilibrium at temperature T. If the dipoles experience an electric field of strength E, then determine the average value of $\cos\theta$ where θ is the angle between the dipole and the electric field. Hint: consider the Boltzmann distribution. Show that if $pE \ll k_BT$ the average of $\cos\theta$ is proportional to E, but if $pE \gg k_BT$ the average of $\cos\theta$ approaches unity. Interpret this last result physically.

The average of $\cos\theta$ is given by using the partition function as

$$\langle\cos\theta\rangle = \frac{\int_0^\pi d\theta\cos\theta e^{-pE\cos\theta/kT}2\pi\sin\theta}{\int_0^\pi d\theta e^{pE\cos\theta/kT}2\pi\sin\theta} = \frac{\int_{-1}^1 dxxe^{pEx/kT}}{\int_{-1}^1 dxe^{pEx/kT}}.$$

Abbreviate $a \equiv pE/kT$, then

$$\langle\cos\theta\rangle = \frac{\int_{-1}^1 dxxe^{-ax}}{\int_{-1}^1 dxe^{ax}} \tag{1}$$

$$= \frac{\frac{\partial}{\partial a}\int_{-1}^1 dxe^{ax}}{\int_{-1}^1 dxe^{ax}} = \frac{\frac{\partial}{\partial a}\frac{1}{a}(e^a - e^{-a})}{(e^a - e^{-a})} \tag{2}$$

$$= \frac{-1}{a} + \frac{(e^a + e^{-a})}{(e^a - e^{-a})} = -\frac{kT}{pE} + \coth\frac{pE}{kT}.$$

The above result is called the Langevin formula.
If $pE \ll kT$, then $\coth a \approx 1/a + a/3$, and we find $\langle\cos\theta\rangle = \frac{pE}{3kT}$. The dipoles are mostly in random order with only a slight tendency to align with the electric field. As E gets stronger, this tendency increases, which increases the value of $\langle\cos\theta\rangle$.
If $pE \gg kT$, $\coth a \approx 1$ so that $\langle\cos\theta\rangle \approx 1$. The dipoles are nearly completely aligned with the electric field. Making E stronger can't increase the alignment any more.

5. Consider the system of two identical plates at $x = \pm a$, each with a surface charge density σ that we studied in class. Starting with the Poisson-Boltzmann equation:

$$\frac{d^2\bar{V}}{dx^2} = -\frac{e^2c(x)}{k_BT\epsilon}, \qquad c(x) = c(0)\exp(-\bar{V})$$

we obtained

$$\frac{1}{2}\left(\frac{d\bar{V}}{dx}\right)^2 - \frac{e^2c(x)}{\epsilon k_BT} = \text{const.}$$

This can be written

$$\frac{1}{2}\left(\frac{d\bar{V}}{dx}(x_1)\right)^2 - \frac{e^2c(x_1)}{\epsilon k_BT} = \frac{1}{2}\left(\frac{d\bar{V}}{dx}(x_2)\right)^2 - \frac{e^2c(x_2)}{\epsilon k_BT}$$

for two positions x_1, x_2.

(a) Take $x_2 = 0$ and $x_1 = a$ because you know the electric field at these two places. Show that

$$c(a) = c(0) + \frac{\sigma^2}{2\epsilon k_B T}.$$

Note that the concentration of counterions at the surface, $c(a)$ never falls below the limiting value $\frac{\sigma^2}{2\epsilon k_B T}$ because if the surfaces are far apart $c(0) \to 0$.
We know $E = -\frac{dV}{dx} = 0$ at $x_2 = 0$ and at $x_1 = a$, $E = -\frac{kT}{e}\frac{d\bar{V}}{x} = \frac{\sigma}{\varepsilon}$.. This means that

$$\frac{1}{2}\left(\frac{-e\sigma}{\varepsilon kT}\right)^2 - \frac{e^2}{kT\varepsilon}c(a) = -\frac{e^2}{kT\varepsilon}c(0),$$

or $c(a) = c(0) + \frac{\sigma^2}{2\varepsilon kT}$
(b) Consider $\sigma = 0.2\text{C/m}^2$ which is typical for a fully ionized surface and which corresponds to one elementary charge per 0.8 nm^2 or 1.25×10^{18} charges per square meter. Given, σ, obtain the limiting value of the concentration $\frac{\sigma^2}{2\epsilon k_B T}$ at the surface. If these counterions are considered to occupy a layer of thickness $\delta = 0.2$ nm, what the charge per unit area, $\frac{\sigma^2\delta}{2\epsilon k_B T}$ does this correspond to? You should find that it is almost the same as the charge density itself. This is an interesting result, for it shows that regardless of the charge density away from the surface, most of the counterions that effectively balance the surface charge are located in the first few angstroms from the surface. (For lower surface charge densities, the diffuse layer extends well beyond the surface.)
The minimum value is $\frac{\sigma^2}{2\varepsilon kT} = \frac{(0.2)^2}{2(80)(8.85\times10^{-12})(1.38\times10^{-23}293} = 7 \times 10^{27}\ \text{m}^{-3}$
$\frac{\sigma^2}{2\delta\varepsilon kT} = 7 \times 10^{27}\ \text{m}^-3(0.2 \times 10^{-9}\ \text{m} = 1.4 \times 10^{18}$ ions per m^2.