3.052 Nanomechanics of Materials and Biomaterials: Spring 2007
Assignment #4 Solutions Due Date:
Thursday 04.24.07
You are encouraged to use additional resources (e.g. journal papers, internet, etc.) but please cite them (points will be deducted for not doing so). You will need to research additional sources to answer some questions. Everything must be answered in your own words; also, do not copy phrases or sentences from the paper or podcast.
+ 5 extra credit for posting a message on one of the podcast message boards.

1. van der Waals Forces at Work : Gecko Feet Adhesion. Tian, *et al.* PNAS 2006 99: 12252-12256.
a. Equation [16] gives an alternative geometry for calculating the van der Waals adhesion force. Define the assumed geometry and all constants according to the schematic in Figure 1i, and then use equation [16] to recreate the plot shown in Figure 4.

ANS. Equation [16] in Tian, et al. (Eq. [1] below) gives the interaction between half a cylinder of radius R and a flat surface;

$$F_{VDW} = \frac{Ab\sqrt{R}}{16\sqrt{2}D^{5/2}} \quad [1]$$

where b is the length of the cylinder, A is the Hamaker constant, D is the separation distance from the bottom of the cylinder to the surface defined in the schematic on the right below. All separation distances are defined perpendicular to the substrate surface (horizontally in the schematics below, what we normally call the *z* direction).
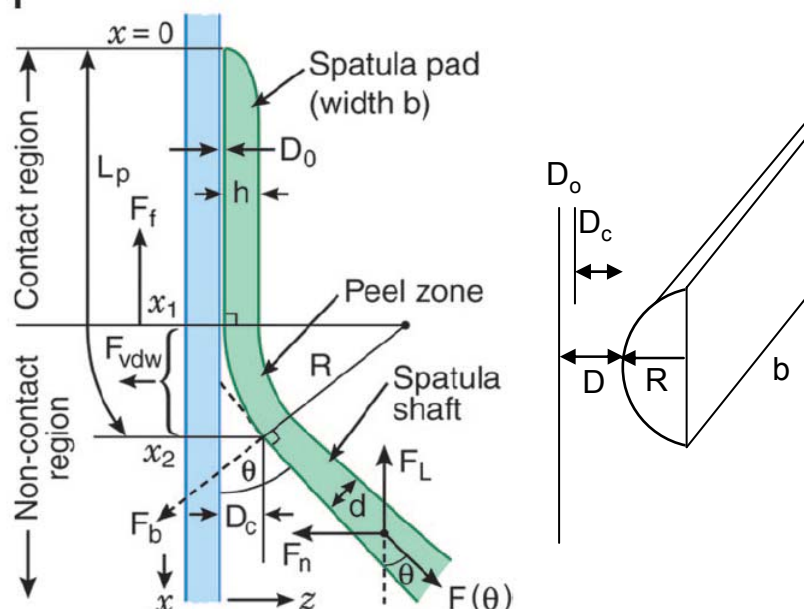
Courtesy of National Academy of Sciences, U. S. A. Used with permission.
Source: Tian, Y., et al. "Adhesion and Friction in Gecko Toe Attachment and Detachment."
PNAS 103, no. 51 (2006): 19320-19325. © 2002, National Academy of Sciences, U.S.A.

Equation [1] is used to approximate the van der Waals interaction in the peel zone where D is approximated as the separation distance between the surface and the bottom of the spatula at x_2;

$$D = D_o + D_c \quad [2]$$

where D_o is the equilibrium separation distance for hard wall contact and D_c is the critical distance from the bottom of the spatula pad at x_1 to the bottom of the spatula pad at x_2. From geometry one obtains eq. [11] of Tian, et al. for D_c;

$$D_c = R\,(1 - cos\theta) \quad [3]$$

where R = the radius of the spatula (which will be set equal to the radius of the cylinder) and θ = the spatula bend angle. Hence, when $\theta = 0°$, $D_c = 0$, $D = D_o$. However, this relationship doesn't hold for small θ, so the authors used an empirical power law (Eq. [12] to relate R and θ:
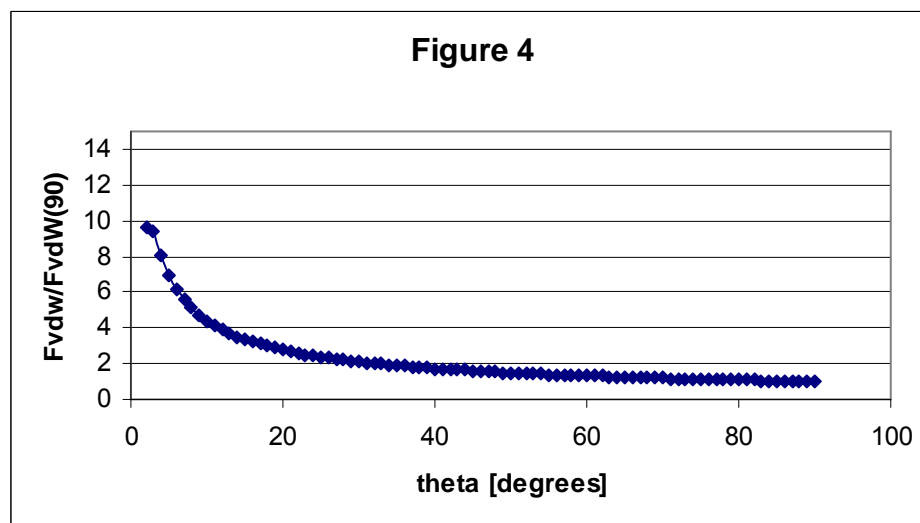
$$R = 4125\theta^{-1.35} \quad [4]$$

Substituting [4] into [3] and [3] into [2] one obtains:

$$D = D_o + 4125\theta^{-1.35}\,(1 - cos\theta) \quad [5]$$

Substituting [4] and [5] into [1] one obtains :

$$F_{vdW} = \frac{Ab}{16\sqrt{2}} \frac{(4215\theta^{-1.35})^{0.5}}{[D_0 + (4215\theta^{-1.35})(1 - cos\theta)]^{2.5}} \quad [6]$$

As given in the paper, the Hamaker constant A = 0.4 x 10^{-19} J, D_0 = 0.3 nm, and b = 200 nm. Use these values in equation [6] to calculate $F_{vdW}(\theta)$ for θ from 0° to 90°, and plot $F_{vdW}(\theta)$ / $F_{vdW}(90°)$ vs. θ to recreate Figure 4.

Figure 4

See the Excel file posted on the MIT Server for graphing details.

b. How do Figures 5 and 6 explain the roll-in, roll-out mechanism for gecko walking?

Figure 6 shows that F_n and F_L are highest at low angles, so that the gecko "rolls in" to low angles, less than 30°, to attach strongly in both friction and adhesion. Figure 5 shows that $F(\theta)$,

the force at which the gecko needs to pull its toes in order to detach from the surface, is lowest at high angles. The gecko "rolls out" to raise the attachment angle up to 90°, where it is easy for it to pull hard enough to overcome the attachment forces due to friction and adhesion, and pull away from the surface.

c. From the Discovery Channel movie on Professor Autumn Kellar
    i. Explain what was meant by "the gecko hairs become one with the wall."

The molecular origin of van der Waals forces is the polarizability of electron clouds of gecko foot atoms with the electron clouds of wall atoms inducing an instantaneous fluctuating dipole which causes an attractive force, essentially causing the gecko foot hairs to "merge" at the atomic level with the wall.

    ii. Explain what was meant by "the gecko is the Bermuda triangle of biology."

This phrase refers to the fact that many different theories have been proposed for gecko adhesion, and that if a scientist were to study one area he/she could get sucked up into a black hole of research and not make any significant progress.

    iii. Name a number of potential applications for the fundamentals behind gecko feet adhesion.

Several potential applications were mentioned in the Discovery Channel video and some are listed here. However, there are potential many more great applications for gecko-like adhesive mechanisms.
- climbing aids ("gecko gloves")
- removable adhesives ("gecko tape")
- search and rescue robots which climb & crawl like geckos
- Mars "gecko rovers"
- Children's toys

    iv. What is the "Mecko Gecko"?

The Mecko Gecko is a robot with sticky feet. The feet do not adhere by van der Waals forces like the gecko, but the robot overall uses some of the same walking principles as the gecko.

    v. Name 3 other types of biological adhesion mechanisms and the animals that use them.

- Secreted biomacromolecular adhesives used by different bugs
- Capillary adhesion used by frogs
- Suction used by salamanders
- Ligand-receptor lock-and-key cell adhesion

2. Boundary Lubrication Podcast: Briscoe, *et al.,* "Boundary Lubrication Under Water."
***Nature* 444, 9 November 2006, 191-194.**
    a. Research 3 different definitions of "boundary lubrication" and 3 different technological applications where boundary lubrication is relevant (cite all sources).

There are several different definitions for "boundary lubrication"; the differences largely stem from the scale of the technological application where the lubrication is relevant. Following is a sampling of definitions chosen at random from solutions submitted by students taking 3.052 this semester:

Definitions of "boundary lubrication"
-- "the reduction of friction and wear between rubbing surfaces with molecular monolayers on the surfaces" (Briscoe, *et al., Nature* 444, 2006: submitted by Amanda Morris)
-- "When a complete fluid film does not develop between two rubbing surfaces, boundary lubrication is necessary to reduce the friction between the surfaces. Because of this non-uniform fluid film, the thickness may be thinner in some regions compared to others which allow dry contact between the wear surfaces. Basic mineral oil is used to create a lubricant that forms a surface film over the surfaces. The most common boundary lubricants are different types of greases because they have the most desirable properties. They not only shear easily but they also flow and dissipate heat easily, and form a protective barrier for the surfaces." (http://www.engineersedge.com/lubrication/boundary_lubrication.htm: submitted by Kimberly Kam)
-- "that condition of lubrication in which the friction between surfaces is determined by the properties of the surfaces and properties of the lubricant other than viscosity. Boundary lubrication encompasses a significant portion of lubrication phenomena and commonly occurs during the starting and stopping of machines." (Encyclopedia Britannica: submitted by Katrine Siversten)

Technological applications relevant to boundary lubrication:
-- "Boundary Lubrication is found *in vivo* in many places, in the body, between the lungs and the chest walls for example. This paper (Hill, B.A., "Boundary lubrication *in vivo*", *Proc Instn Mech Engrs* 214(H):83-94, 2000; http://journals.pepublishing.com/content/732p123613t3848w/fulltext.pdf) is a summary of boundary lubrication *in vivo*. The information from this paper can be used to develop better implants and prosthetics, such as in the second source, where it is applied for making artificial joints.(http://www3.interscience.wiley.com/cgi-bin/fulltext/62500305/PDFSTART)" (submitted by Siamrut Patanavanich).
-- Boundary lubrication is important to the design of mechanical ball bearings between moving parts in many types of machinery. (http://books.google.com/books?hl=en&lr=&id=k4fgJRho0M0C&oi=fnd&pg=PR15&dq=%22boundary+lubrication%22+technological+applications&ots=ZM-KO3CAv9&sig=dolY0eR6qpyzZoGJw4ff0NDCPO0 : book link submitted by Elaine Lee)
-- "Boundary lubrication is important most machines during startup and shutdown. This is the case with piston rings in engines. Teeth and saliva are another example. The barrel of gun needs to be oiled for the bullet. (http://www.me.utexas.edu/~bryant/courses/me383s/DownloadFiles/LectureNotes/BoundaryLubrication.pdf)" (submitted by Fredrick Porter).

Professor Klein proposes that ions can behave as "molecular ball bearings" in boundary lubrication. Explain this analogy.

Ions in solution are surrounded by water molecules in a hydration layer. It takes a great amount of energy to remove this hydration layer, but it is believed that water molecules within the hydration layer can very easily exchange with each other for very little energetic cost. This

means that hydrated ions create large normal repulsive forces between surfaces but can actually be very fluid in shear, leading to low shear forces. In this way they act as "molecular ball bearings".

b. Prof. Klein mentioned that "one can not take pictures with the SFA" (like the AFM can). In a few sentences, explain why not.

One cannot image with the SFA because the SFA involves two crossed cylinder surfaces (radius of ~1 cm each) interacting with each other rather than one surface and one very small probe tip as in the AFM. It is the small size of the AFM probe which enables imaging. Interactions measured in the SFA are averaged over the entire contact area, which is generally around 1000 µm^2.

c. Professor Klein states that "experiments are meaningless without controls" and refers us to Figure 1 which is a control experiment. Explain in ~0.5 page what these data show and exactly <u>how they verify the accuracy of their experimental setup</u>.
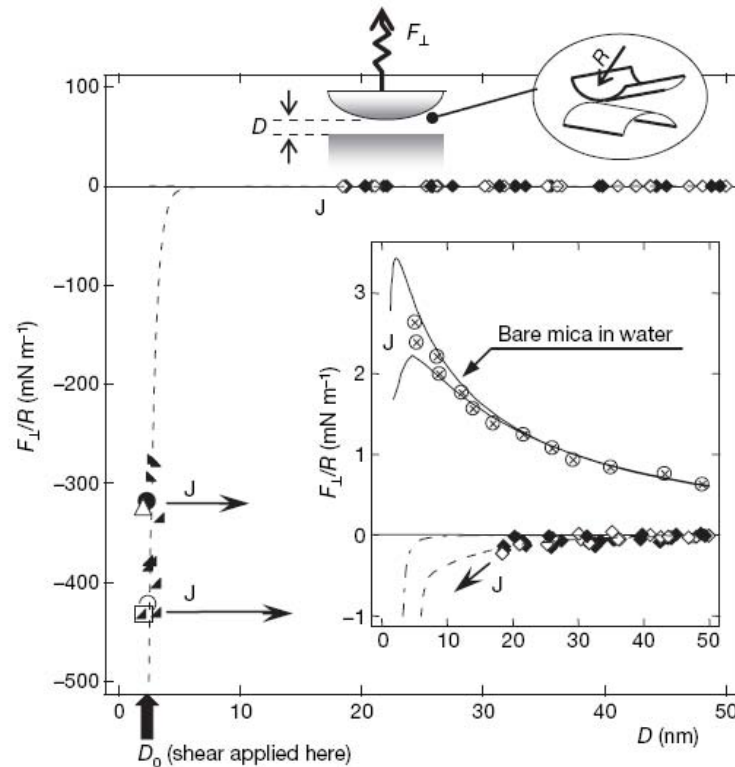
Courtesy of Jacob Klein. Used with permission.
Source: Briscoe, W. H., et al. "Boundary Lubrication Under Water." *Nature* 444 (November 9, 2006): 191-194.

The data in the inset of figure 1 show the expected interactions for bare mica surfaces interacting with each other. The data should be well described by DLVO theory, which accounts for the two forces at play: a repulsive electrostatic force due to negative charges on the mica surface, and an attractive van der Waals force. As the theoretical DLVO curves do fit the data quite well, the authors had confirmation of the expected behavior of the SFA under known conditions and could use such such knowledge as a control for experiments with surfactant-coated surfaces.

d. The bare mica data from Figure 1 has been digitized and is posted on the MIT Server in an Excel file. Given the theoretical parameters provided in the Figure caption, estimate a

quantitative value of the Hamaker constant using two separate DLVO theoretical predictions; 1) constant surface charge and 2) constant surface potential. Include in your solutions a single plot showing the theoretical fits compared to the experimental data.

DLVO theory combines contributions to interaction potentials stemming from both electrostatics and van der Waals interactions: $F_{DLVO}(D) = F_{EDL}(D) + F_{vdW}(D)$

First, define the van der Waals portion of the equation. In Lecture 11, page 6, the van der Waals

interaction between two crossed cylinders is given as: $W(D) = -\dfrac{A\sqrt{R_1 R_2}}{6D}$

Differentiating gives the force between crossed cylinders:

$$\frac{F(D)}{R} = -\frac{1}{R}\frac{\partial W(D)}{\partial D} = -\frac{A\sqrt{R_1 R_2}}{6D^2 R} = -\frac{A}{6D^2}$$

$R = R_1 = R_2 \sim 1$ cm (see Figure 1 caption).
Hamaker constant = $A = \pi^2 C\rho^2 \sim 10^{-19}$ J (typical value)

The electrostatic double layer contribution can be estimated using two different boundary conditions for crossed cylinders. Using a linearized Poisson-Boltzmann formulation, both can be expressed as $F = \kappa RZe^{-\kappa D}$, where the prefactor Z depends on the boundary condition chosen. For a constant surface potential ψ_0, (see Slide 3 of Lecture 16)
$Z = 9.38 \times 10^{-11} \tanh^2(\psi_0/107)$ [=] J·m^{-1} ; ψ_0 is in mV

From the Figure 1 caption, $\psi_0 = 155$ mV. This is above the accepted threshold (60 mV) for linearizing the Poisson-Boltzmann formulation, so our fits may not be as accurate as those made in the paper using the full non-linear solution.

For $\psi_0 = 155$ mV, $Z_{\psi 0} = 9.38 \times 10^{-11}$ J·m^{-1} * $\tanh^2(155/107) = 7.52 \times 10^{-11}$ J·m^{-1}.

For a constant surface charge σ, Z must be converted according to the following equation relating σ and ψ_0 (also from Lecture 16, slide 3): $\sigma = 0.116 \sinh(\psi_0/53.4)\sqrt{c_0}$ [=] C·m^{-2} ; c_0 is in moles/L.

Rearranging gives $\psi_0 = 53.4 \arcsin h\left(\dfrac{\sigma}{0.116\sqrt{c_0}}\right) = 53.4 \cdot \ln\left(\dfrac{\sigma}{0.116\sqrt{c_0}} + \sqrt{\dfrac{\sigma}{0.116\sqrt{c_0}} + 1}\right)$

Plugging into the equation for Z gives the following equation for Z at constant surface charge σ:

$$Z_\sigma = (9.38 \times 10^{-11} J \cdot m^{-1}) \tanh^2\left[\frac{53.4}{107}\ln\left(\frac{\sigma}{0.116\sqrt{c_0}} + \sqrt{\frac{\sigma}{0.116\sqrt{c_0}} + 1}\right)\right]$$

where c_0 units are moles/L and σ units are C·m^{-2}.

From the Figure 1 caption, $\sigma = 0.0048$ C·m^{-2} and $c_0 = 1.5 \times 10^{-5}$ M. This gives $Z_\sigma = 7.051 \times 10^{-11}$ J·m^{-1}.

The Debye length, κ^{-1}, is determined by the properties of the solution in which the experiments are performed, which is noted in the caption of Figure 1 to contain 1.5×10^{-5} M 1:1 background electrolyte. This defines the Debye length as $\kappa^{-1} = 0.304/[NaCl]^{0.5} = 0.304/(1.5 \times 10^{-5})^{0.5} = 78.5$ nm.

The full curves are then described by the formula

$$\frac{F_{DLVO}}{R} = \kappa Z e^{-\kappa D} - \frac{A}{6D^2}$$

The given κ and Z will not give a good fit to the experimental data, since, as noted above, the surface potential is above the threshold for acceptable linearization. However, it is possible to achieve good fits by leaving both the Debye length and the Hamaker constant as free fitting parameters. This was done in the attached Excel file to achieve the following fits:
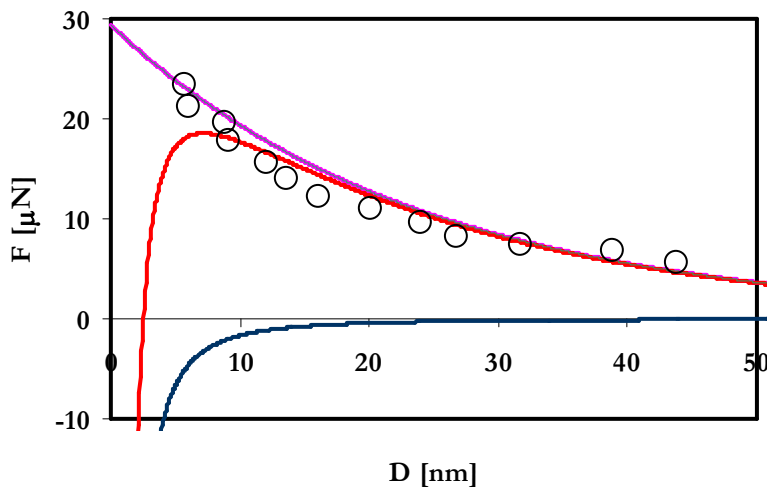
Constant surface potential: $\psi_0 = 155$ mV; **A** = 10^{-19} J; $\kappa^{-1} = 28$ nm

Constant Surface Potential
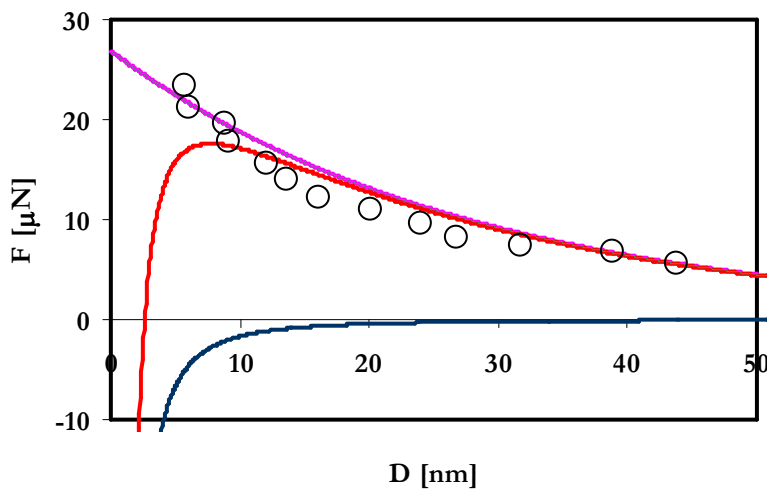
Constant surface charge: $\sigma = 0.0048$ C·m^{-2}; **A** = 10^{-19} J; $\kappa^{-1} = 24$ nm

Constant Surface Charge

D [nm]

e. The boundary lubrication mechanism presented in the current paper differs slightly from that proposed in Klein's previous paper on fluidity of bound hydrated ionic layers (Raviv, et al. 1540 297 2002 *Science*). Explain how.

In the case of boundary lubrication in this paper, it appears that water molecules (probably only two molecular layers thick) have slipped in between the polar headgroups of the amphiphilic detergent molecules involved and the mica surface and that the hydrated ions are fixed and fairly immobile via ionic interactions with the substrate. In the current paper, Klein proposes that the slip plane is between the hydrated polar head groups and the mica surface.

3. The Electrostatic Double Layer / Cartilage Podcast: Dean, et al. " Compressive Nanomechanics of Opposing Aggrecan Macromolecules" *J. Biomech.* 2006 39,14 2555.

a. For Figure 6a and b, why isn't the constant compliance regime set to D=0? Explain how this nonzero distance of the constant compliance regime is determined experimentally in <0.5 pages.

The constant compliance regime is not set to D=0 because the distance where constant compliance is reached depends upon the structure of the aggrecan layers at each different ionic strength. In the experiments, Dean *et al.* used AFM height images to measure the compressed height of the aggrecan layers at the maximum force applied in the force-distance measurements; they treated this height as the non-zero constant compliance offset.

b. For Figures 6a and b calculate the distance at which repulsion due to conformational entropy begins for each salt concentration and summarize these values in a table. Compare the values obtained in the table for Figures 6a and 6b and explain any differences.

Repulsion due to conformational entropy can only come into play when the aggrecan layers actually come into physical contact with each other. This would occur a 2 × the uncompressed (zero force) height of the aggrecan layer, h_o for a single aggrecan layer and $2h_o$ for two opposing aggrecan layers, which would be dependent on salt concentration). These values can be approximated as the total range of interaction, which is equal to the distance at which force rises above noise (D_r) minus the range of the electrostatic double layer ($5\kappa^{-1}$), as tabulated below.

Debye length = κ^{-1} = 0.304 / $[NaCl]^{0.5}$ [=] nm when [NaCl] is in moles/L. (This equation was given in recitation; it comes from the Israelachvili text and is just the result of calculating

$$\kappa^{-1} = \sqrt{\frac{\varepsilon RT}{2F^2 c_0}}$$ for the parameters specific to [NaCl].)

Ionic Strength [NaCl]	κ^{-1}	Figure 6a		Figure 6b.,	
		D_r	$h_o = D_r - 5\kappa^{-1}$	D_r	$2h_o = D_r - 5\kappa^{-1}$
0.001 M	9.6	800	752	900	852
0.01 M	3.04	400	385	700	685
0.1 M	0.96	300	295	600	595
1 M	0.3	150	148.5	280	278.5

c. Given the chemical structure and dimensions of aggrecan and GAG and the aggrecan molecular surface packing density reported in the paper, estimate the areal surface charge per unit area (C/m^2) due to the GAGs at pH 5.6 (the pH at which the nanomechanical experiments were carried out).

ANS. The packing density of aggrecan on planar substrates was cited in the paper (page 2557) as ~ 1 aggrecan per 25 nm x 25 nm area = 625 x 10^{-18} m^2.

One aggrecan is made up of ~ 100 GAGs attached covalently to a core protein, where each GAG has about 100 negative charge groups, as can be seen from the structure given in Lecture 16, slide 5: GAGs are about 45 nm in length, which corresponds to ~ 50 disaccharides, each of which carries a -2 charge at pH 5.6 (since pH 5.6 is well above the pKa of the carboxyl and sulfate groups on the GAG molecule). This means each GAG chain carries a negative charge of around -100. At 100 GAGs per aggrecan, this is -10^4 charge per aggrecan. One charge carries -1.602 x 10^{-19} C (charge on an electron).

From the total charge on all 100 GAGs per aggrecan, and the area per aggrecan, we can calculate the charge per unit area:

Areal surface charge due to GAGs = $\sigma_1 = \dfrac{-10^4 \times 1.602 \times 10^{-19}\, C/aggrecan}{\left(25 \times 10^{-9}\right)^2 m^2/aggrecan} \cong -2.56\, C/m^2$

d. Given the known amino acid sequence of the protein core backbone and the aggrecan molecular surface packing density reported in the paper, estimate the areal surface charge per unit area (C/m^2) due to the core protein at pH 5.6 (the pH at which the nanomechanical experiments were carried out). You may want to prepare a Matlab script to assist in the calculation. What is the percentage contribution to the total areal surface charge per unit area?

Based on the chemical structure of the 20 amino acids, the possible charged amino acids at pH = 5.6 are (assuming a particular amino acid is charged when $|pH - pI| \geq 2$)

Amino Acids	Counts	pI	Charge
Ala (A)	161	6.00	0
Asp (D)	106	2.77	-1
Glu (E)	257	3.22	-1
Lys (K)	25	9.59	1
Arg (R)	72	11.15	1
His (H)	29	7.47	0/1

The known sequence of the aggrecan core protein, available from the Swiss Protein Data Bank (http://ca.expasy.org/cgi-bin/niceprot.pl?P16112), and linked from the Nanonewton webpage citation on aggrecan (http://www.cmb.lu.se/ctb/html/Aggrecan.htm), gives us the number of charged residues within the core protein.

You can use several methods to count the number of charged residues in the aggrecan core protein sequence; using "find and replace" in Word to count is perhaps the easiest way. This yields the following sequence data:

Negatively charged residues: -1 x 106 D residues + -1 x 257 E residues = -363

Positively charged residues: +1 x 29 H residues + +1 x 25 K residues + +1 x 72 R residues = +126

Total charge: -363 + 126 = -237

In Coulombs, total charge = -237 x 1.602 x 10^{-19} C = -3.80 x 10^{-17} C

If histidine is assumed not to carry a charge, then the total charge drops to -266 x 1.602 x 10^{-19} C = -4.26 x 10^{-17} C

It is also possible to count the numbers of each charged residue using a Matlab script; an example is given below.

Since there is one aggrecan core protein in 25 nm x 25 nm area, the core protein areal surface charge = -237 x 1.602 x 10^{-19} C / (25 x 10^{-9} m)^2 = = 0.061 C/m^2 (with charged histidines) or -266 x 1.602 x 10^{-19} C / (25 x 10^{-9} m)^2 = = 0.068 C/m^2 (without charged histidines).

Total surface charge per unit area is then the sum of the core protein and GAG contributions; the percentage of charge coming from the core protein is 0.061 / (2.56 + 0.061) * 100 = 2.33% (with charged histidines) or 0.068 / (2.56 + 0.068) * 100 = 2.59% (without charged histidines).

Matlab script for charge count:

```
function [n] = ChargeCount(seq)
cols = length(seq);
n = 0;
 for i = 1:cols,
     if strcmp(seq(i),'D') == 1 || strcmp(seq(i),'E') == 1,
         n = n-1;
     elseif strcmp(seq(i), 'K') == 1 || strcmp(seq(i),'R') == 1,
         n = n+1;
     elseif strcmp(seq(i), 'H') == 1,
         n = n+1;
     end
 end
```

Matlab script for number of amino acids count:

```
function [n] = AACount(seq)
 cols = length(seq);
 n = zeros(6,1);
 for i = 1:cols,
    if strcmp(seq(i),'A') == 1,
        n(1) = n(1) + 1;
    elseif strcmp(seq(i),'D') == 1,
        n(2) = n(2) +1;
    elseif strcmp(seq(i),'E') == 1,
        n(3) = n(3) + 1;
    elseif strcmp(seq(i),'K') == 1,
        n(4) = n(4) + 1;
    elseif strcmp(seq(i),'R') == 1,
        n(5) = n(5) + 1;
    elseif strcmp(seq(i),'H') == 1,
        n(6) = n(6) + 1;
    end
 end
```

e. Based on your answers to parts c. and d., can the linearized Poisson-Boltzmann Debye-Huckel formulation be employed to predict the EDL force? Why or why not?

The linearized Poisson-Boltzman Debye-Huckel formulation is made with the assumption that surface potentials or charges are small; in lecture 16, slide 3, the guideline is given that surface potential should be less than 60 mV to use the linearized approximation. At an electrolyte concentration of 0.1M, a surface potential of 60 mV corresponds to a surface charge of $\sigma = 0.116 \sinh(\psi_0/53.4)\sqrt{c_0} = 0.116 \sinh(60/53.4) \sqrt{0.1M} = \sim 0.0016$ C/m^2. At ~2.5 C/m^2, the surface charges per unit area on aggrecan are far above this guideline. The linearized approximation should not be used in this case.

+ 5 extra credit for posting a message on the podcast message board.