

# 3.052 Spring 2007 General Message Board

## Albert Park - More Gecko Robots

May 2nd, 2007

It looks like the mecko gecko has some competition! And this time there are actually going to be gecko-style spatula on the feet

<http://www.technologyreview.com/Infotech/18602/>

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## (Pantea Khodami) What is the origin of the banding periodicity in collagen?

April 30th, 2007

This is quite an interesting and controversial question. Some of you may remember this concept from the 3.034 rat tail tendon lab when we reviewed the structure of collagen type I. I have posted a detailed response here :

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## Hashem Dabbas : Lecture 16, Slide 6, Are the aggrecan standing up in the nanomechanical experiment as they are drawn, what is the height of the aggrecan?

April 15th, 2007

ANS (Prof. Ortiz). I think this was the question that was asked, but it was hard to hear on the mp3. If not, let me know. So the height of the aggrecan will decrease with increasing salt concentration due to screening of intramolecular electrostatic repulsion (which promotes chain extension via overcoming configurational entropy driving the polymer to a random coil). The fully extended contour length of aggrecan is ~400 nm. One question on your pset is to estimate the height of the aggecan layer at each salt concentration in these data using your knowledge of EDL theory.

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## John Rogosic: In vivo are the aggrecan oriented as they are in the nanomechanical experiment?

April 15th, 2007

ANS (Prof. Ortiz). This is a great point that in vivo aggrecan are oriented fairly randomly in 3D compared to the in vitro experiments where each layer is chemically end-grafted in a more-or-less 2D layer. It should be noted that the aggrecan are not all standing up straight as drawn in the schematic, but the initial uncompressed height will decrease with increasing ionic strength due to screening of intramolecular electrostatic repulsion and hence, with thermal motions and increasing compression one would expect the experimental system and GAG orientation to look pretty random and increasingly more like the in vivo 3D system.

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## Kyle Yazzie : . Since charged groups give biological materials like cartilage their stiffness, is there any correlation between the number or density of charged groups in an active person's cartilage vs. a sedentary person's cartilage (everything else being equal)?

April 15th, 2007

ANS. (Prof. Ortiz & Prof. Grodzinsky (EECS)). There are many papers which state that cartilage is thicker and has a higher "fixed charge density" in "loaded" regions compared to "non-loaded" regions of articulating joints. For example, In animals in which joints are immobilized, GAG content goes down. See the Introduction in this paper for citations on this topic; Sah, et al. J. Orthop. Res. 1989 7:619-636.

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## Chris Bruce : When do constant potential versus constant charge conditions hold in Poisson-Boltzmann EDL Theory?

April 15th, 2007

ANS. (Prof. Ortiz & Prof. Grodzinsky (EECS)). For most biological surfaces and molecules (e.g. proteins, polysaccharides), charge is the electrical parameter of interest, in that one can either control it is controlled by the pH and ionic strength of the adjacent electrolyte solution through dissociation/titration. It is possible to maintain constant charge, for example, as long as the solution pH is sufficiently far away from the pKa of the surface groups. However, it should be noted that the interaction itself may locally altering the pH and ionic strength such that the local conditions alter the ionization state, thereby changing the surface charge.

For metal/electrolyte interfaces (e.g., metal surface, metal nanoparticle, and certain colloidal and electrode surfaces such as a silver-silver chloride–electrolyte interface and its many cousins), the potential across the surface can be controlled using an electrode attached to the metal with respect to a reference electrode in the electrolyte. Similarly, the potential at a silver chloride surface is controlled by the chloride concentration in the electrolyte bath via a Nernstian relation; same for other similar colloidal interfaces where the surface is a sparingly soluble salt in which one of the ions is also in the solution phase.

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**Anonymous.** I think it's just the idea of controlling the distance vs. leaving it free, as in the other class we discussed it in terms of stabilizing particles by keeping them far apart, where increasing ionic strength would shield repulsion of like charged nanoparticles

April 8th, 2007

Ans. (Prof. Ortiz) If the particles are left free, i.e. with no externally applied compressive force, then the EDL and VDW potentials will balance each other out and the particles will sit at an equilibrium distance apart. This is exactly analogous to the equilibrium bond length in the LJ potential, except in the LJ potential the repulsive term is the  $r^{-12}$  short range overlap of electron clouds. In this sense the EDL repulsion is stabilizing the particles because it is preventing VDW collapse/aggregation. You are correct that increasing ionic strength will shield the EDL interaction and cause a reduction in the equilibrium distance until collapse/aggregation occurs. We will go over why this is in the next Lecture #15.

If we were to compress this system with an external force, then an increasing repulsive force would take place due to deviation of the EDL away from its equilibrium separation distance.

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**Anonymous :** You mentioned in class today that at longer distances there was no interaction, but in another class we discussed classical electrostatic repulsion between the two charged surfaces, shielded by the ions, thus at long ranges we talked about a repulsive force based on the electrostatics of the 2 double layers repelling each other.

April 8th, 2007

Ans. (Prof. Ortiz) OK, so remember the question on the pset, "Why is the range of an interaction an ambiguous concept?" The answer was because in reality the interaction only goes to zero as the separation distance  $D \rightarrow \infty$ . A practical definition for the range of the EDL interaction is  $5 \cdot \kappa^{-1}$  (Debye Length) (we will go through why this is in Lecture #15 on Tuesday). EDL \*is\* generally considered a long range interaction because it is of the order of a few to hundreds of nm depending on the solution bulk ionic strength. Hence we can consider the EDL's to interact and cause a marked interaction when the sphere-surface, sphere-sphere, or surface-surface separation distance becomes smaller than  $5 \cdot \kappa^{-1}$ . For  $D > 5 \cdot \kappa^{-1}$  we can assume the interaction is negligible.

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**Anonymous:** In your formulation, are the water/counterions allowed to flow out between the surfaces?

April 8th, 2007

Ans. (Prof. Ortiz) No they are not allowed to flow out, we are considering two surfaces which are semi-infinite and impermeable, which is a good approximation for solid spheres in which the radius,  $R_{tip} \gg$  tip-surface or sphere-sphere separation distance. Formulations can be made for semi-permeable surfaces as well by using appropriate boundary conditions which would change the counterion density profile, the potential, and magnitude of the repulsive force as a function of compression.

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**Anonymous:** In another class I am taking, the definitions of the [electrical] double layer differed a little I think. [It was] discussed as a more tightly bound layer of counter-ions, while I think you're including a lot more loosely bound ions to the surface.

April 8th, 2007

**Ans. (Prof. Ortiz)** OK, this is my guess at the apparent discrepancy. I think this is just a terminology issue and depends on what length scale you are looking at the system from. Our perspective is at quite a small length scale, a very close up view of the charged surface where we can see all the individual ions. From this perspective the counterion EDL is diffuse and not directly bound to the surface like the Stern layer. However, if you were zoom far out and think of the system at a much larger length scale, the EDL would look tightly bound to the surface.