# 3.052 Nanomechanics of Materials and Biomaterials :
Spring 2007 Final Exam

1. **Single Macromolecule Force Spectroscopy**. (Data taken from: Oesterhelt, et al. *New J. Physics* 1 (**1999**) 6.1-6.11)). Figure 1 shows four different single molecule stretching experiments (each colored line is a different experiment) for poly(ethylene glycol) (PEG) chemically end-grafted to a planar surface taken with a "bare" unfunctionalized silicon nitride atomic force microscope in aqueous solution. L_f is the bridging polymer chain length = tip-sample separation distance at which the polymer detaches from the probe tip.
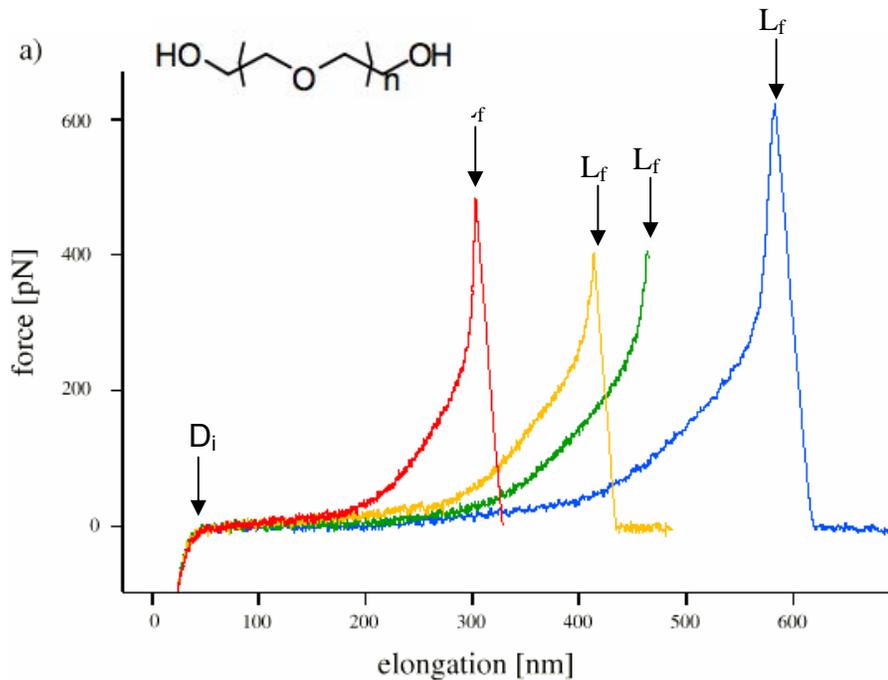
Figure 1.

(a) **Molecular Fingerprint of PEG (15 pts)**
(i) Does the inextensible FJC (a=7Å, $L_f = 0.99 L_{contour}$) overestimate or underestimate the experimentally measured single molecule stretching force at intermediate elongations? (quantitative numerical calculations are needed).

(ii) Pose a possible explanation for the deviation observed in (a) based on the known conformation of PEG in water. Clarify whether the origin of this deviation is expected to be entropic or enthalpic. (**10 pts**)

(b) **Short Answer** : **Properties obtained from Force-Elongation curve (answer questions based on the data provided in Figure 1).**
(i) Calculate a numerical value for the average adhesion force between the probe tip and a single molecule of PEG. Explain how this value was obtained.

(ii) What is the height of the undeformed PEG layer? Explain how you obtained this value. What is the primary source of error in this value? (**5 pts**)

(iii) Why is there a large distribution of values for L_f observed for different experiments? (**5 pts**)

2. **Nanoindentation.** Below is a plot of AFM-based nanoindentation data taken on bone which appears today(!) online in the journal *Nature Materials* (Tai, Ortiz, et al.- see press release on MIT News website). Each colored set of symbols is a different nanoindentation experiment on the same sample.
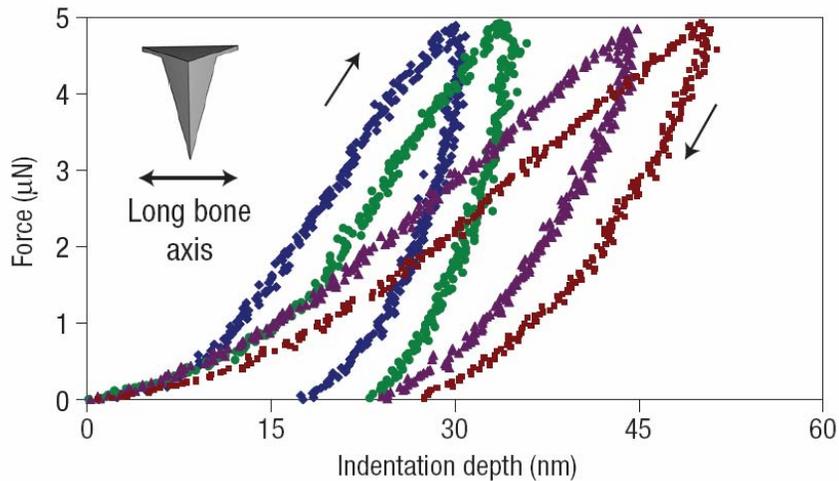

Figure 2.

(a) Estimate the average value of the modulus for the four experiments presented in Figure 2, you can approximate the geometry of the probe tip as a cone with an included conical angle, α = 24.5°. The contact area for a conical indenter is defined as A=$\pi h_c^2 \tan^2\alpha$.(**15 pts**)

(b) Why is the value obtained for (a) not equivalent to the elastic Young's modulus (as defined by the slope of the traditional stress versus strain curve)? (**5 pts**)

(c) Does this sample undergo inelastic deformation? Why or why not? (**5 pts**)

(d) One important experimental parameter to consider is the spacing between neighboring indents when carrying out multiple nanoindentation experiments. Explain why in one or two sentences based on the data in Figure 2. (**5 pts**)

(e) How is the zero position (force, displacement) determined in AFM-based nanoindentation? (5 pts)

3. **Electrical Double Layer and Cartilage.**
   (a) Below is a Figure from the podcast paper Dean, et al. *J. Biomech.* **2006**. These are AFM height images taken with a bare unfunctionalized silicon nitride probe tip of a microcontact printed surface of cartilage aggrecan in aqueous salt solution. The salt concentration for each image is given underneath the image. Explain the trends observed in terms of the EDL. (**10 pts**)
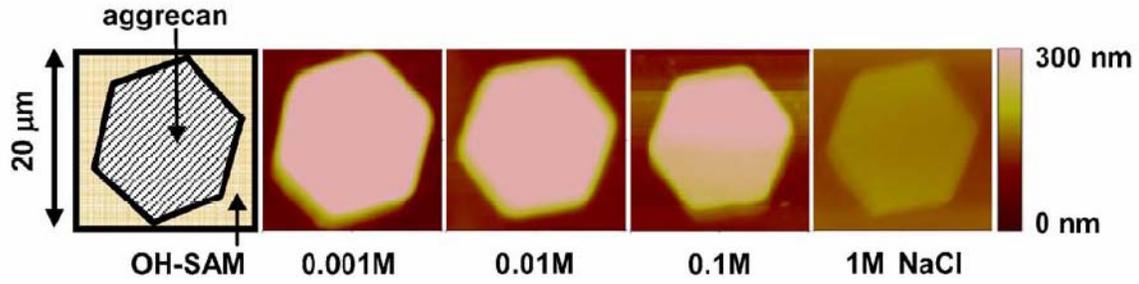
Figure 3.

(b) Derive a theoretical equation (**force** versus distance) for the compression of a cartilage aggrecan brush taking into account van der Waals interactions, steric repulsion, and EDL defining all parameters. Explain which physical parameters in your equation are the most important for controlling each constituent interaction. (**15 pts**)

HAVE A GREAT SUMMER!

Hydrophilic Chemical Groups

hydroxyl groups -OH

carbonyl groups

carboxyl groups -   can ionize to COO⁻
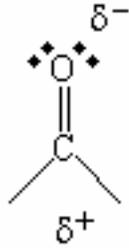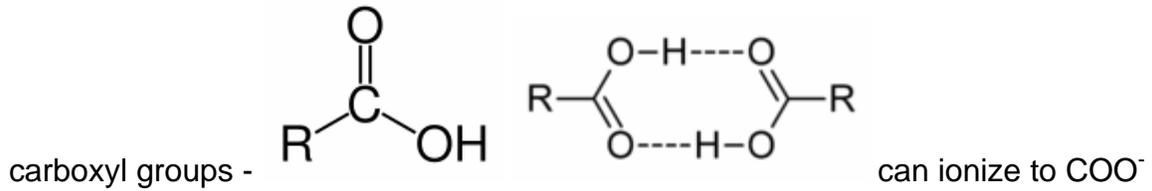
sulfates : SO_4^-
sulfonates : SO_3^-

aldehydes

ketones

alcohols
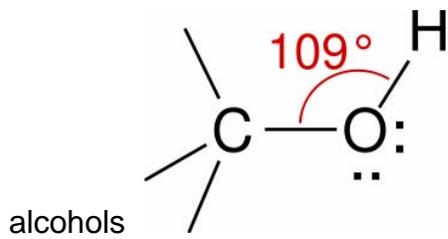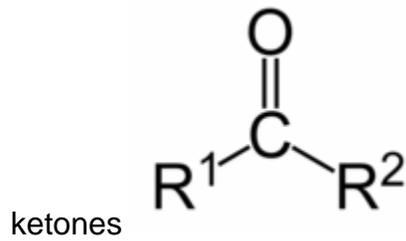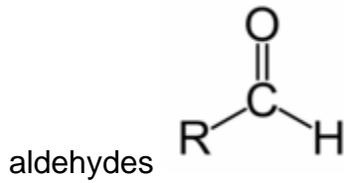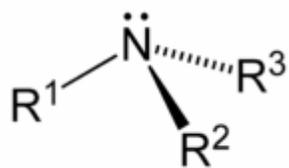
amines
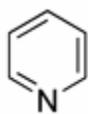
N-heterocyclic rings

Amides
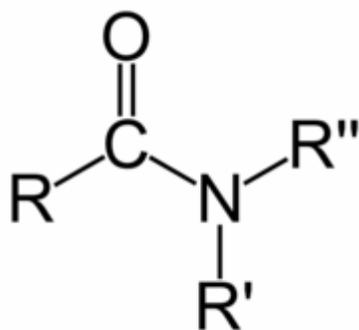
O-heterocyclic rings
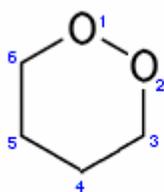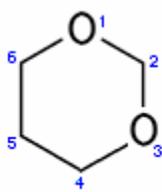
1,2-dioxane   1,3-dioxane   1,4-dioxane

2
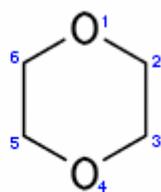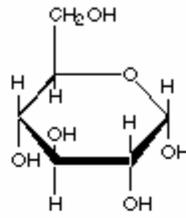
Monosaccharides
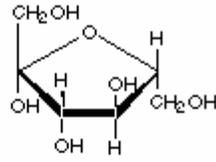
α–Glucose

Fructose

Disaccharides
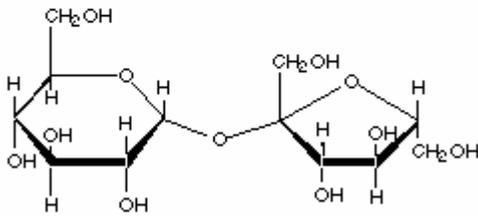
Sucrose
(glucose (α1-->2) fructose)
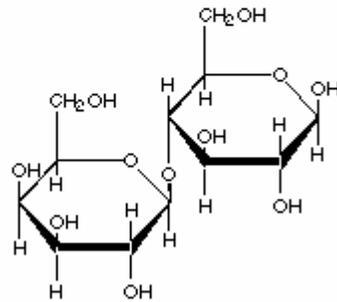
Lactose
(Galactose (β1-->4) Glucose)

Hydrophobic Chemical Groups

methyl -CH_3
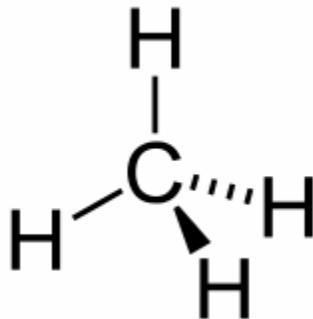

alkanes   Alkanes can be linear (general formula
C_nH_{2n+2}) where the carbon atoms are joined in a snake like structure, cyclic
(general formula C_nH_{2n}, n>2) where the carbon backbone is linked so as to form
a loop, or branched (general formula C_nH_{2n+2}, n>3)
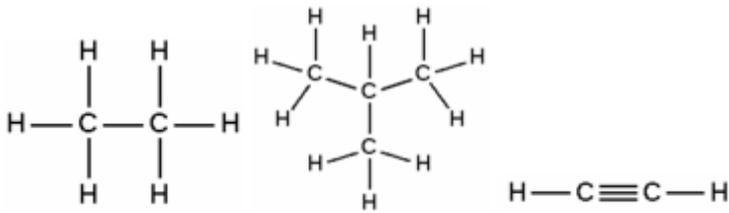
hydrocarbons

Fatty acids : mostly hydrophobic, but have hydrophilic COOH at end

Butyric	(butanoic acid):	$CH_3(CH_2)_2COOH$	C4:0
Caproic	(hexanoic acid):	$CH_3(CH_2)_4COOH$	C6:0
Caprylic	(octanoic acid):	$CH_3(CH_2)_6COOH$	C8:0
Capric	(decanoic acid):	$CH_3(CH_2)_8COOH$	C10:0
Lauric	(dodecanoic acid):	$CH_3(CH_2)_{10}COOH$	C12:0
Palmitic	(hexadecanoic acid):	$CH_3(CH_2)_{14}COOH$	C16:0
Stearic	(octadecanoic acid):	$CH_3(CH_2)_{16}COOH$	C18:0
Arachidic	(icosanoic acid):	$CH_3(CH_2)_{18}COOH$	C20:0
Behenic	(docosanoic acid):	$CH_3(CH_2)_{20}COOH$	C22:0

Amino acids with hydrophobic side groups
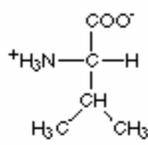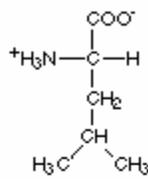
Valine (val)   Leucine (leu)   Isoleucine (ile)   Methionine (met)   Phenylalanine (phe)
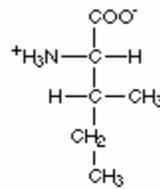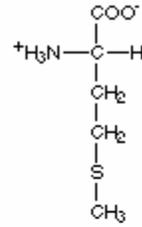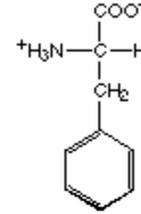
Amino acids with hydrophilic side groups
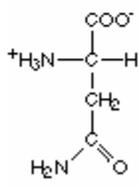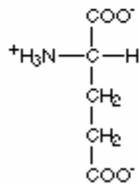
Asparagine (asn)   Glutamic acid (glu)   Glutamine (gln)   Histidine (his)   Lysine (lys)   Arginine (arg)
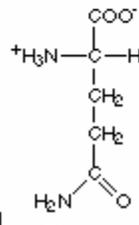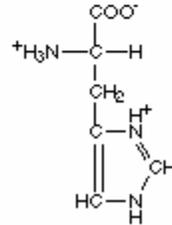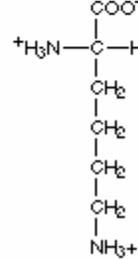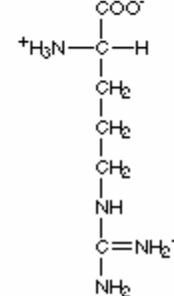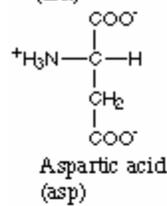
Aspartic acid (asp)

Amino acids that are in between
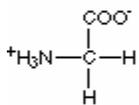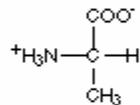
Glycine (gly)   Alanine (ala)   Serine (ser)   Threonine (thr)   Tyrosine (tyr)   Tryptophan (trp)
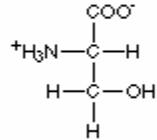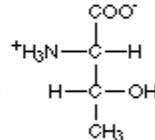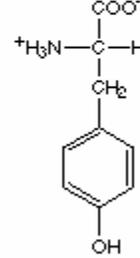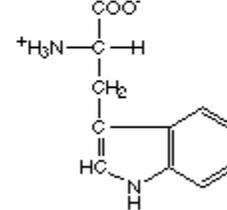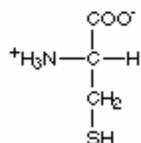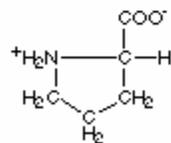
Cysteine (cys)   Proline (pro)

Amphiphilic Molecules

5

Lipids
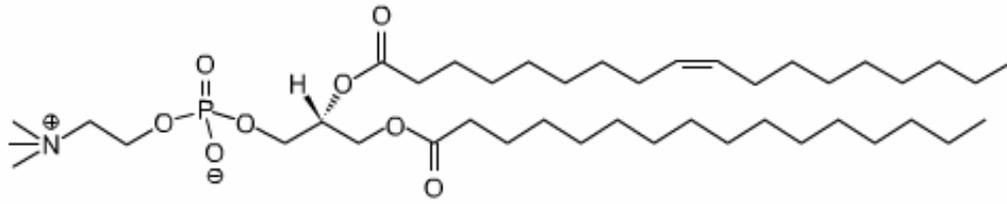
Cholesterol
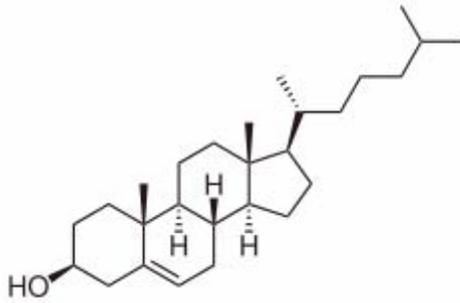
Cholic acid

Polyethylene glycol