Question 1

A (6p)

A concentrated dispersion of polystyrene colloids in 0.1 mM NaCl with radius 50 nm is stabilized by -NH$_3^+$ groups on the surface. If a 100 μm thin layer is sheared between two plates, how fast must they move relative to each other to observe substantial shear-thinning? You may use the relations:

$$\kappa = \left[\frac{2C_0 e^2}{\varepsilon\varepsilon_0 k_B T} \right]^{1/2}$$

$$\text{Pe} = \frac{6\pi\eta_0 R^3}{k_B T} \frac{\partial e}{\partial t}$$

First calculate the Debye length, which should be 31 nm (water at room temperature). Next calculate for which shear rate the Péclet number reaches unity. The radius to be inserted should be 81 nm because the Debye length needs to be added. This should give $\partial e/\partial t = 416$ s^{-1}, which means that the plates should move with a velocity of 4.2 cm/s.

Mean score: 3.46

B (4p)

Soluble charged polymers (polyelectrolytes) are added to a dilute dispersion of the same colloids. It turns out that this causes the colloids to aggregate (flocculation) if they are negatively charged, but *also* if they are *positively* charged. Describe why aggregation occurs and the mechanism in both cases.

The negatively charged polymer will "bridge" the positive colloids, i.e. several colloids stick to the same polymer molecule. The positively charged polymer causes aggregation by "depletion interactions" or osmotic pressure, i.e. since they cannot approach close to the colloids more volume is liberated for them when the colloids stick together.

Mean score: 1.29

Note: Many people talked about "ions" screening the charges on the colloids. I am not sure why. Polymers with multiple charges, not ions, were added to the colloids.

Question 2

A (6p)

The following polypropylene (-CH(CH$_3$)-CH$_2$-) melts are cooled down to room temperature (which is below T_m):

Melt ↓ Property →	Stereochemistry	Branching points
A	isotactic	none
B	syndiotactic	none
C	random	2

Your task is to make an educated guess about the degree of crystallinity in each melt after cooling. For A, B and C, choose three of the following values:

0% 10% 30% 60% 100%

You must motivate your guesses!

Polymers are never 100% crystalline so this value can be excluded. A complete absence of crystals is also essentially impossible under T_m. The isotactic stereochemistry means all sides point in the same direction, which promotes crystal formation. Random stereochemistry is the worst for crystallization to occur. Branching also makes it harder for crystals to form. Thus the answer should be A: 60% B: 30% C: 10%

Mean score: 3.25

B (4p)

Polypropylene can be rubbery at room temperature (T_g is around 0 °C) because the crystals cross-link the molecules. The density is 0.9 g/cm^3. Assume that the crystallinity is 10% and that all lamellae have a thickness of 12 monomers. For simplicity, also assume that the strands cannot go through the same lamellae more than once.

Under these assumptions estimate Young's modulus:

$$Y = \frac{3\rho k_B T}{mN_{part}}$$

The trick is to know the meaning of the formula and the lamellae structure. The monomer mass is 42 g/mol. If the crystallinity is 10%, this amount of monomers are present inside 2D lamellae. If each strand encounters a new lamellae every time, the number of monomers between each "cross-link" must on average be $N_{part} = 0.9 \times 12/0.1 = 108$. Using the formula with consistent units then gives $Y = 1.5$ MPa. (In reality the strands often go back into the same lamellae.)

Mean score: 1.46

Question 3

Atomic force microscopy can be used to pull out single polymer molecules that are attached to both the surface and the scanning probe. The instrument gives the force based on the deflection of the cantilever holding the probe. (Zero force means that nothing is attracting or repelling the probe.) The following shows the force during *retraction*, with several experiments of the same type in different colors:
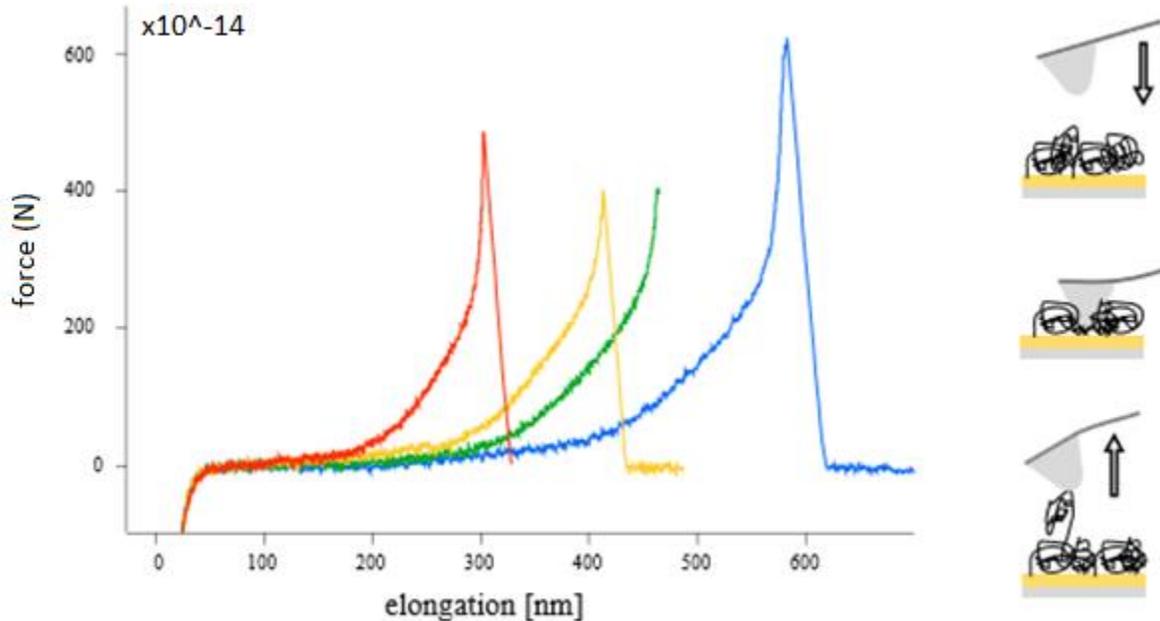
(Note that the values on the y axis are $\times 10^{-14}$.) You may assume the point where the polymer is attached to the surface corresponds to an elongation of zero. You may also assume the freely jointed chain model works:

$$G(r) = \frac{3k_{\mathrm{B}}Tr^2}{2Na^2} + \text{constant}$$

A (3p)

Why are the curves different? Hint: Consider the schematic!

Each time a strand of different length will represent the connection between tip and surface. It is not necessarily the end terminals of the polymer which attach to the tip and the surface and/or the polymers have different molecular weights. The curves look different because the length of the strand which is being pulled (the part of the full polymer) influences the "spring constant".

Mean score 2.25

B (4p)

Estimate the Kuhn length!

Use the entropic spring model. Derive $G(r)$ with respect to r to get the force and once more to get the "spring constant" of $3k_BT/[Na^2]$. Rescaling gives this spring constant as $3k_BT/[abN]$ instead, which should be equal to the slope of the force-elongation graph. Further, aN is simply the contour length, which should be well approximated as the point where the force goes to infinity and the molecule is released. Thus one can solve for b. For the longer strands the spring constant is a bit smaller as expected (higher aN). The answer should be somewhere in the range 2.0-2.5 nm regardless which graph is used.

Mean score: 1.36

Notes: Almost nobody solved this problem but many attempts were fairly rational which gives some points. However, the Flory radius or the random walk only gives the expected end to end distance of an unperturbed coil. It is tricky to implement because here they are being pulled!

C (3p)

The authors claim that at high enough extension the polymer undergoes structural changes on the atomic scale by breaking bonds with the surrounding solvent. Why does the data indeed suggest this?

The derivative of force with respect to elongation is not constant as it should be according to the purely entropic spring model. Instead the derivative of force with respect to elongation increases for high elongation. This suggests that there is some other kind of free energy cost, more than just the entropic coil contribution. (In the article presenting the data, Oesterhelt et al. New Journal of Physics 1999, the scaling of the force axis is different because the entropic contribution is actually very small compared with the enthalpic solvent bonds, but the principle is the same.)

Mean score: 0.57