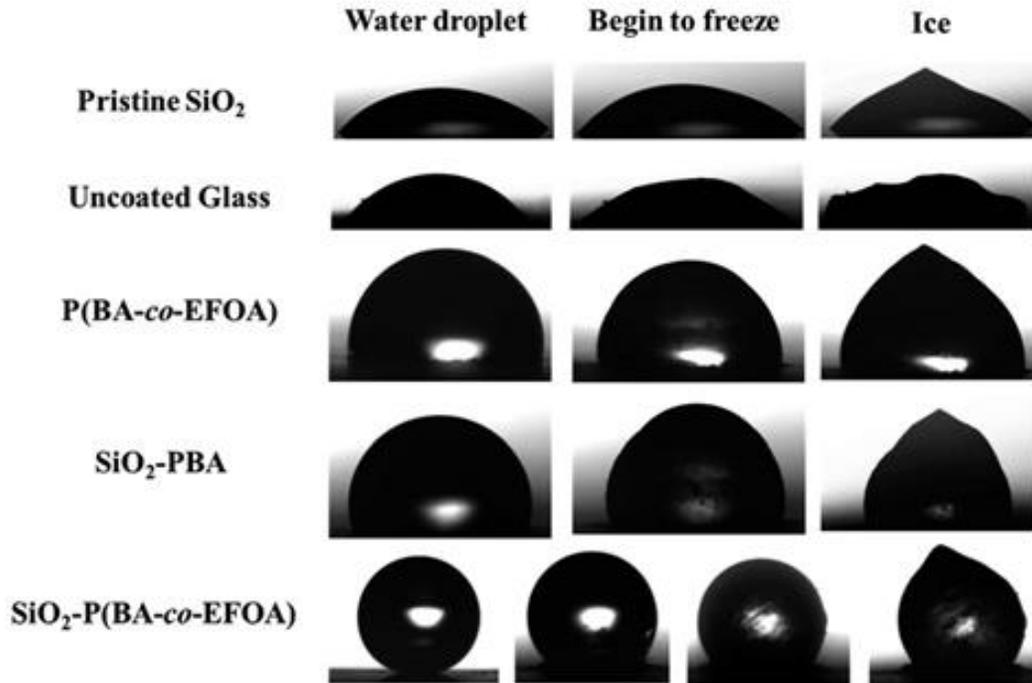**Question 1** (10p)

Cold weather causes many problems because of *icing*, i.e. ice formation on wet surfaces. Much research efforts are devoted to developing materials or surface modifications that reduce icing. The figure below shows small water droplets which freeze on different types of glass surfaces, some modified with polymer brushes.

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Your task is to estimate <u>how much less likely</u> (a dimensionless factor) icing is to occur on the most hydrophobic surface (lowest images) compared with a hydrophilic one (pristine SiO$_2$) if the surface temperature is -100°C. Use a water-ice interfacial energy of 0.03 J/m^2, an ice melting enthalpy of 335 Jg^{-1} and a density of 930 kgm^{-3}.

Some relations that may be useful are:

$$\Delta G^*_{\text{hom}} = \frac{16\pi \gamma_{\text{SL}}{}^3 T_{\text{m}}{}^2}{3\rho^2 \Delta H_{\text{m}}{}^2 \Delta T^2}$$

$$\frac{\Delta G^*_{\text{het}}}{\Delta G^*_{\text{hom}}} = \frac{[1-\cos(\theta)]^2[2+\cos(\theta)]}{4}$$

Hints: The images suggest that the ice nucleation site, which initially forms inside the droplet, has the same shape as the final crystal. You may also assume that the nucleation follows basic Arrhenius kinetics.

The activation energy for homogenous nucleation is not surface dependent and can be calculated since all parameters are given. (The undercooling is 100 K and $T_m = 273$ K.) This gives $\Delta G^*_{\text{hom}} \approx 15 k_B T$. To get ΔG^*_{het} we need the contact angles which are (roughly) 30° and 150° for the hydrophilic and hydrophobic surfaces respectively, which gives 0.19kBT and 14kBT. For basic Arrhenius kinetics the relative increase in probability of nucleation is then simply the Boltzmann factor $\exp(14 - 0.19) \approx 10^6$. So the freezing should become on the order of one million times less likely.

Sidenote: In the paper the surface temperature was only -18 °C and freezing was only a factor of ~100 slower on the modified glass. Our model seems not good enough…

Question 2

A (4p)

Solid colloids are suspended in a water solution with 2 mmolL^{-1} of the salt CaCl$_2$. Calculate the Debye length! You may use the relation:

$$\kappa = \left[\frac{e^2}{\varepsilon \varepsilon_0 k_B T} \sum_i v_i^2 C_{0i} \right]^{1/2}$$

The expression contains only natural constants, $\varepsilon = 80$ for water and assuming $T = 300$ we only need the concentrations and valencies of the ions: $v = -1$ and $C_0 = 4$ mmolL^{-1} as well as $v = 2$ and $C_0 = 2$ mmolL^{-1}. Inserting all values should give $\kappa^{-1} = 4.0$ nm.

B (6p)

The colloids have a radius of 100 nm and are stabilized by sulphate groups (SO$_4^{2-}$) on the surface. A <u>repulsive</u> force of 100 pN was measured between two colloids at a distance (surface to surface) of 10 nm. How many sulphate groups are there on each colloid? Assume there are no adsorbed ions. You may use the relations:

$$P(d) = 2 \frac{\sigma^2}{\varepsilon_0 \varepsilon} \exp(-\kappa d)$$

$$F(d) = -2\pi \frac{R_1 R_2}{R_1 + R_2} \kappa^{-1} P(d)$$

The expression for the force should be used to calculate the osmotic pressure. $R_1 = R_2 = 100$ nm gives $P = 7.99\ldots \times 10^4$ Pa (κ from previously). Use the other formula to get surface charge density $\sigma = 0.0187$ Cm^{-2} (strictly speaking with minus sign). This needs to be converted into number of sulphate groups which carry two elementary charges each. This gives ~0.058 groups per nm^2. Using the area of a colloid this gives a total of ~7300 groups.

Question 3

A (3p)

Polystyrene is often used as a packaging material or as plastic cups. The structure is:
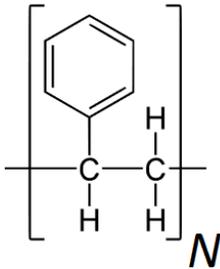
Polystyrene dissolves well in acetone. Calculate the end to end distance if $M = 20$ kgmol^{-1}. In acetone the Kuhn length is 1.0 nm and the monomer length is 0.3 nm.

The monomer weight is $m = 104$ gmol^{-1} which gives $N = 192$. Using the Flory radius with rescaling gives $R = 1^{2/5} \times 0.3^{3/5} \times 192^{3/5} = 11.38\ldots$ nm.

B (4p)

Describe qualitatively the microstructure (molecular arrangement) and the mechanical properties of the material which will form if the acetone evaporates!

A melt will form, but due to the high glass transition temperature the polymers are entangled and stuck. The material is like a brittle solid. (As mentioned it is used for drinking cups and thus it should not be viscous on ordinary timescales.)

C (3p)

The height of a polystyrene brush in acetone is half of the contour length of the coils. What is the grafting density? You may use the relation:

$$H = \left[\frac{\Gamma}{3}\right]^{\frac{1}{3}} a^{\frac{5}{3}} N$$

The contour length is aN, so $H = aN/2$. This is an actual brush height, but the right hand side a and N must still be rescaled. This gives $aN/2 = [\Gamma/3]^{1/3} b^{2/3} aN$ and thus $\Gamma = 3/8$ nm^{-2}.

Note that it is the Kuhn length which matters while a and N disappear.

Question 4

A (2p)

Why does an increase in temperature usually promote mixing of different compounds?

This follows from the entropy of mixing. The number of microstates generally increases for mixed macrostates. Boltzmann's fundamental formula thus gives positive entropy of mixing and with higher temperature the $-T\Delta S$ term increases.

B (4p)

Give one example when an increase in temperature does <u>not</u> promote mixing of different compounds (excluding solids) and explain qualitatively why!

Sometimes introducing a foreign molecule in a pure liquid forces the surrounding molecules to adopt a certain configuration, which reduces the number of microstates. The entropy of mixing can then become negative. The most common example is the introduction of hydrophobic molecules into water or certain hydrophilic polymers.

C (4p)

Give one concrete example of how a concept or theory in soft matter physics can be used to better understand a phenomenon or structure in molecular biology.

This question has many possible answers. Some examples are how the behavior of DNA can be understood by polymer physics, charge screening etc. Another classic would be self assembly of amphiphiles to form biological membranes, with the geometry promoting bilayer structure.