F. Biomaterials

No. 1

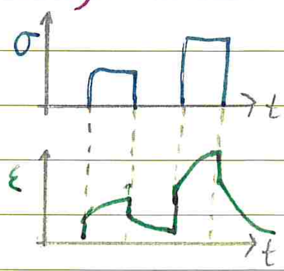
Date 30 . 4 . 19

- A biomaterial is one that comprises part of a living structure or a biomedical device that augments / replaces natural functioning.
- Biomaterials often have much smaller embodied energies and carbon footprints, as well as being recyclable.
- Natural materials are mainly made of C, H, O, N with small amounts of Ca, P, Fe.
- Biomaterials tend to be highly anisotropic because they are often composites.
- Only tend to work at ambient temperatures.

Materials selection

- When a stress is applied to a linear-elastic material, it instantly becomes strained. $\tau = G\gamma$
- However, polymers may have behaviour more similar to liquids, in which the flow rate depends on the stress
  ↳ for a Newtonian fluid, strain rate $\propto$ stress
  $\therefore \tau = \eta \frac{d\gamma}{dt}$ where η is the viscosity (Pa.s)

- In reality, materials exist on a spectrum of viscoelasticity.
- Organic materials tend to have 3 strain components:
  1. Elastic
  2. Viscous flow
  3. Slow recovering



- These materials can be modeled as combinations of springs (linear elastic solids) and dashpots (ideal liquids). e.g

↳ $\varepsilon = \varepsilon_d + \varepsilon_s \quad \therefore \quad \dot{\varepsilon} = \dot{\varepsilon}_d + \dot{\varepsilon}_s$

$\Rightarrow \dot{\varepsilon} = \frac{\sigma}{\eta} + \frac{\dot{\sigma}}{K} \Rightarrow K\dot{\varepsilon} = \frac{1}{t_R}\sigma + \dot{\sigma}$

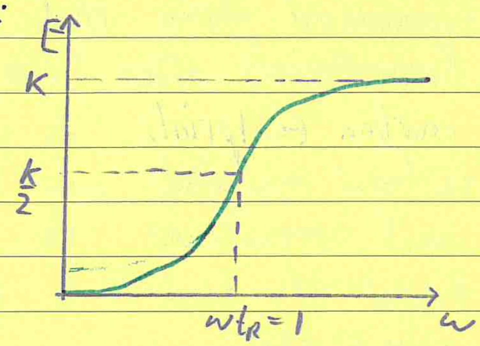
relaxation time $t_R = \frac{\eta}{K}$

(Maxwell model)

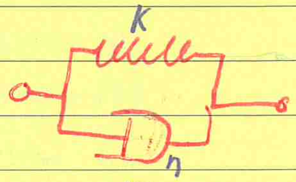
- We can impose an oscillating stress $\sigma = \sigma_0 e^{i\omega t}$ which will cause a strain $\varepsilon = \varepsilon_0 e^{i(\omega t - \phi)}$:

$$\Rightarrow E = \frac{k\omega^2 t_R^2}{1 + \omega^2 t_R^2}$$

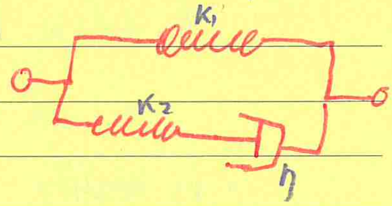
$$\tan\phi = \frac{1}{\omega t_R}$$



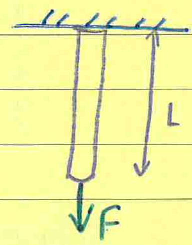
- at high freq, there is no time for viscous flow so the material behaves like a linear elastic solid. $E \to k$, $\phi \to 0$
- at low freq, spring is negligible compared to dashpot. Behaves like an ideal liquid. $E \to 0$, $\phi \to \pi/2$
- at intermediate frequency, some strain will be recovered but energy will be dissipated.



- The Voigt model is more accurate for constant stress – some time dependance, but $\varepsilon \to$ constant.
- However, it doesn't work well at high freq because E is dominated by the dashpot. The standard linear solid model improves this.



Selecting materials for strength



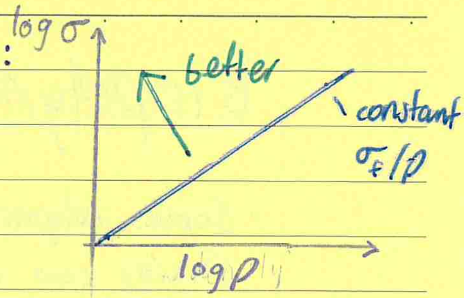
- Suppose we want to choose the lightest material for a wire of length L that must support a load F:
  - the materials properties to be considered are the failure strength σ_f and density ρ.
  - the thinnest wire that can be used has

$$\sigma_f = \frac{F}{\pi r^2} \quad \text{and} \quad \rho = \frac{m}{\pi r^2 L} \xrightarrow{\text{eliminate } r^2} m = LF\frac{\rho}{\sigma_f}$$

materials properties.

  - thus to minimise mass we maximise the merit index σ_f / ρ
  - r was not specified in the problem so was eliminated as a free variable.

- We can then look at a strength-density map:
  - contours of constant merit can be plotted
  - in this setup, woods and steels are similarly 'good', but spider silk is the best.



- Consider a rectangular cantilever of fixed length & width. Suppose we want to minimise mass for a given load:
  - at the top of the root $\sigma_f = \frac{Eh}{2R} = \frac{Mh}{2I} = \frac{6LF}{wh^2}$
  - eliminating h gives a merit index of $\sqrt{\sigma_f}/\rho$
  - this has a gradient of 2 on the log-log scale.

Selecting for stiffness

- e.g Minimise the deflection of a square cantilever with mass m.

$$\delta = \frac{FL^3}{3EI} = \frac{4FL^3}{Eh^4} \text{ and } \rho = \frac{m}{Lh^2} \Rightarrow \delta \sim \frac{\rho^2}{E}$$

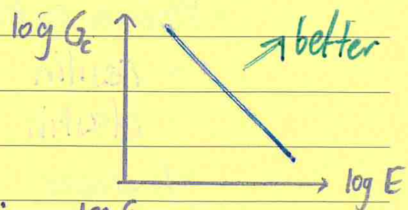
∴ maximise the merit index $\sqrt{E}/\rho$

- Woods perform very well here.

Selecting for toughness

- To maximise resistance to an impact, we just need max G_c.
- To maximise the tensile load without crack propagation:

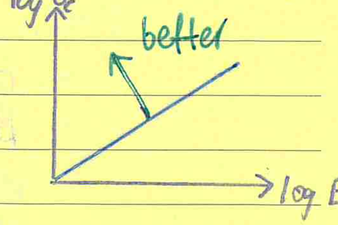
$$\sigma_f = \sqrt{\frac{EG_c}{\pi c}} \quad \therefore \text{ maximise } \sqrt{EG_c}$$



↳ this is the fracture toughness K_c
↳ good materials include bone or antler

- To maximise tensile strain without crack propagation:

$$\varepsilon_f = \frac{\sigma_f}{E} = \sqrt{\frac{G_c}{\pi c E}} \quad \therefore \max \sqrt{\frac{G_c}{E}}$$



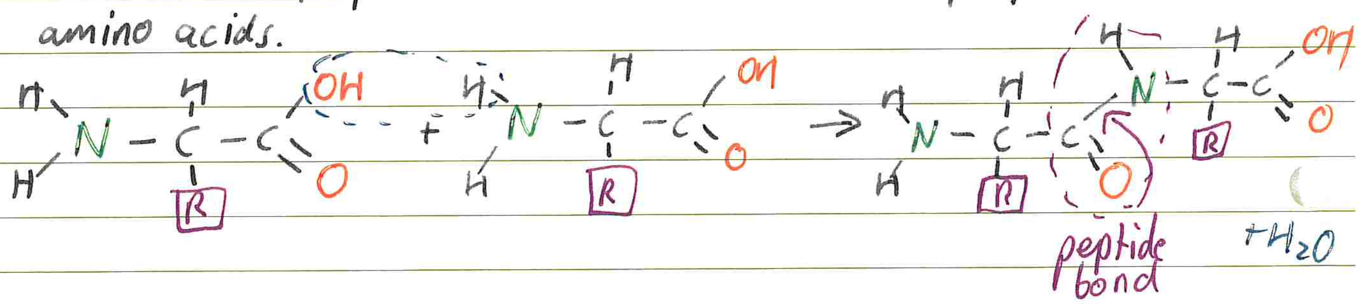
↳ best material for this is skin.

Biopolymers

- Some polymers can show large recoverable strain because coiled chains can uncoil then return to lower energy conformation.
  - ↳ must be sufficient energy for bond rotation
  - ↳ chains must not slide past neighbours
- Natural rubber can be improved by vulcanisation to add sulfur crosslinks.
- Elastic behaviour depends on coiling rather than changing bond lengths: "entropy spring".
  - ↳ at high temp, rubber becomes stiffer again because $G = H - TS$, so ~~increasing~~ decreasing S by stretching the polymer results in $G\uparrow$.

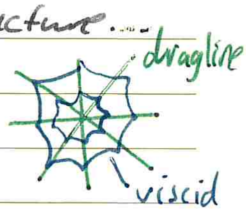
Proteins

- Proteins are polymers made from condensation polymerisation of amino acids.



- Protein rubbers are randomly coiled cross-linked chains of proteins.
  - resilin has excellent elastic properties, found in insect wing hinges
  - elastin is found in vertebrates, e.g human skin / neck ligaments.
- However, because of the hydrogen bonding between N-H and C-O, proteins can fold into compact conformations:
  - α-helix: right-handed helix with pitch ~5Å
  - β-sheet, i.e straightened chains lying in a plane.
  - very easy to transition between α and β because the H bonds can be broken by ↑ temp or making it wet.

- Keratin is an α packed protein when dry, but β when wet.
  - hence wet hair can be shaped
  - chains already stretched and heavily crosslinked. Thus, keratin is strong and stiff.
- Spiders can produce dragline silk and viscid silk (among others)
  - both have the same chemistry but different microstructure....
  - dragline silk is 25% β-sheet micelles: very high tensile strength / mass, used to support spider weight.
  - viscid silk is less crystalline and hence less stiff, but has a low coefficient of restitution - useful to catch insects.

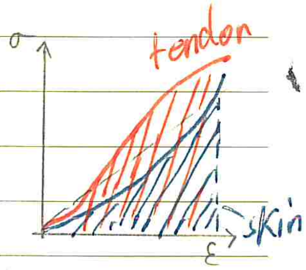


- Collagen is a protein fibre found in all multicellular animals
  - a collagen 'molecule' is made of three left-handed polypeptide helices coiled in a right-handed sense
  - these molecules arrange in a staggered pattern with covalent crosslinks to form fibrils that are stiff and strong.

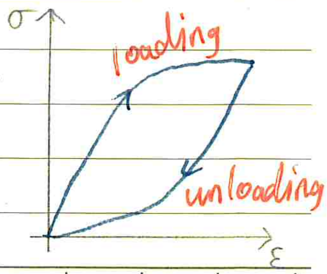
  - fibrils are packed into fibres, in parallel bunches
- Skin is a composite made of collagen fibres in an elastin matrix
  - fibres may have a preferential orientation : skin is anisotropic
  - different types of skin have different proportions of collagen/elastin.

Elastic energy storage

- Biomaterials rarely have a linear stress-strain curve
- Skin gets stiffer when stretched. This means that less energy is stored so crack propagation is harder.



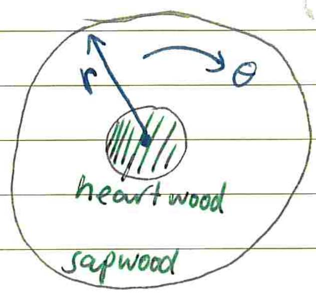
- But materials that need to store more energy may have more convex curves, e.g tendon
- Because biomaterials are viscoelastic, input elastic energy is not completely recovered: elastic hysteresis
  ↳ more area in loop ⇒ more energy absorbed during deformation, i.e tougher.



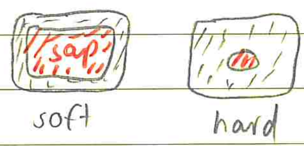
- Modelling a material as linear elastic, a merit index for energy storage is σ_f^2/E
- However, if we are interested in stored energy that can be returned, we must include the coefficient of restitution R (a.k.a 'resilience).

Structural polysaccharides

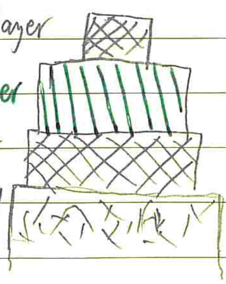
- Wood is mostly made of vertically aligned elongated cells, with some additional radial cells.
  - ↳ highly anisotropic
  - ↳ can be analysed in cross section, radial section, or tangential section z↑→θ.



- In softwood, vertical cells are for support and conduction, with radial cells used for storage.
- In hardwood, vertical cells only support – there are specialised cells (vessels) for conduction.

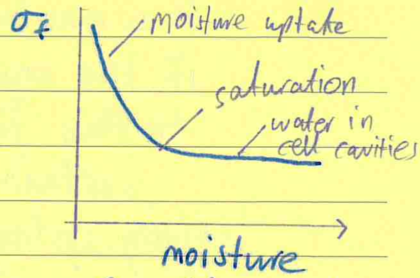


- The cell walls are a composite consisting of cellulose fibres in a lignin matrix. The insides are essentially voids.
- Cellulose is a polymer chain built from glucose units
  - chains are packed into small bunches
  - bunches stack together to form crystalline microfibrils
  - these microfibrils are separated by amorphous lignin, which makes up 50% of the material.
- The cell wall has multiple layers, the thickest being the middle layer which contains near-vertical fibres and is the main contributor to stiffness.



- Tensile stiffness can be modeled with the Voigt model – but the 'voids' should be included.
- Wood is much weaker in compression because of its fibres. Cell walls can buckle, causing creases which can become cracks in tension.
  - ↳ trees solve this by putting outer layers in tension, so much more compression can be tolerated.

- Wood's strength is strongly affected by moisture:
  - ↳ water helps break the H bonds between cellulose chains, which become more mobile.
  - ↳ varying moisture content can cause dimensional change.



- Wood is very tough; in addition to fibre pullout, separation of the middle and outer layers is very energy intensive.

Chitin

- Chitin is similar to cellulose: nitrogen-containing polysaccharide
  - ↳ stronger H bonds ∴ chitin is stronger and stiffer than cellulose.
- Chitin is the main structural material in exoskeletons, but it achieves its strength and hardness without incorporating minerals.
- Toughness similar to cortical bone.

Biominerals

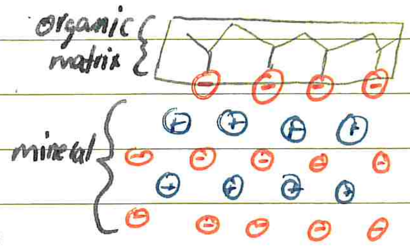
Non-structural biominerals

- Some bacteria are magnetotactic: they contain ferromagnetic crystals whose size, shape, and orientation are well controlled by proteins.
  - ↳ this allows the bacteria to orient themselves
- The inner ear contains small calcite crystals which move around within fluid and interact with small hairs – used for balance.

$CaCO_3$ for structural materials

- $CaCO_3$ is the main component of seashells, though a significant amount of Ca may be replaced by Mg.
- The main solid phases are: amorphous, calcite, aragonite.
  - ↳ though calcite is more energetically stable, especially when there are Mg^{2+} ions, both can be made to precipitate.

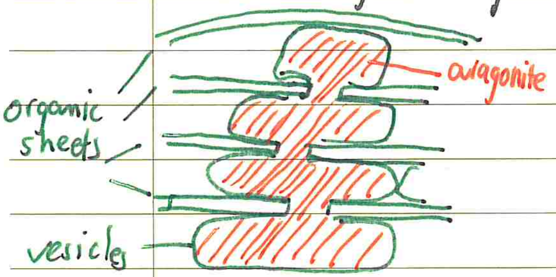
- It is easiest to nucleate a mineral structure if the organic template is well-matched
  - ↳ thus living systems can encourage certain minerals to precipitate.



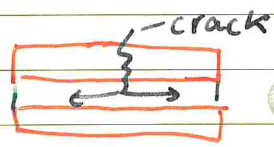
- Living systems also control ion transport and can thus specify the chemical composition.
- Constrains in growth geometry can lead to crystallographic texture (preferred directions), like in metal casting.

Nacre (mother of pearl)

- Nacre is a composite of organic protein sheets and aragonite.
- The aragonite grows to fill predefined vesicles in the organic matrix.
  - ↳ this growth results in either a 'brick wall' or 'stack of coins' structure



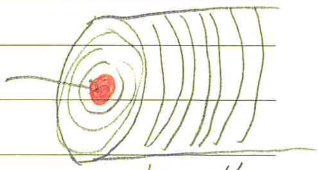
- Though aragonite is very brittle, nacre is tough:
  - G_c 1000x greater
  - K_c 10x greater (because E is lower in nacre).
- Nacre's toughness is a result of crack deflection:
  - when an aragonite plate is cracked, the crack will then deflect along the weak organic layers ⊥ to plane of advancing crack
  - this creates large new surface areas, absorbing energy.



Biomedical materials

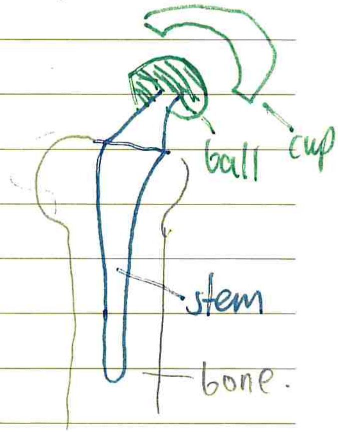
Bone

- Bone is a composite of collagen (soft) and hydroxyapatite, a hard mineral based on calcium phosphate.
  - ↳ collagen fibres are interleaved with HA crystals to form a lamellar structure
  - ↳ lamellar sheets wrap around the Haversian canal, a blood vessel, to form an osteon →
  - ↳ these osteons are then bundled together to form the walls ~~of~~ in cortical bone.



- Bone has reasonable tensile strength and stiffness (longitudinally), and is very tough — much tougher than artificial ceramics.
- Cancellous / spongy bone is less stiff: found at the ends of bones, its stiffness matches the cartilage layer so that stresses are shared.
- The body produces bone where it is needed
  - ↳ conversely, if bones are not subjected to stress, they are resorbed. Problematic for astronauts.

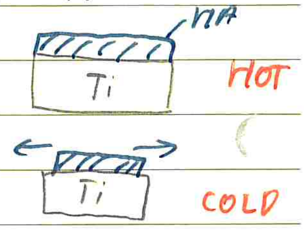
Artificial hip joints



- Metals are generally chosen for the stem:
  - ceramics are too brittle; polymers suffer from fatigue
  - blood is quite corrosive → need to choose metal that is biocompatible (nontoxic) and inert
  - e.g titanium, stainless steel.
- Material cannot be too stiff, otherwise it will bear most of the load and bone may resorb
  - ↳ use a porous Ti alloy, made by sintering, which is less stiff.

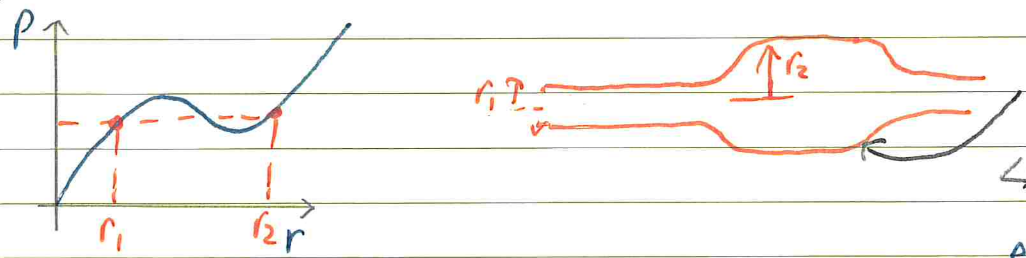
- The ball and cup require low friction and resistance to wear.
  - metal on metal has low wear but debris are metallic and may be a health risk.
  - current research involves ceramics, but they wear more easily.

- The stem is bonded to the bone by coating it with hydroxyapatite
- A problem is that the HA coating cracks off the metal:
  - HA coating is applied by plasma spraying (i.e very hot)
  - because HA has a greater coeff of thermal expansion, it will be under tensile stress when cooled to room temp
  - this can be improved by alloying the Ti with manganese, which has higher α.

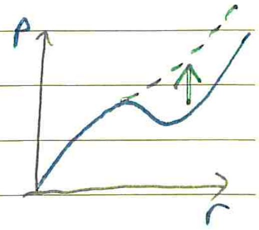


Arteries

- Arterial walls are a composite of collagen and elastin
- One problem is aneurysms:
  - the pressure ~~force~~ in an artery can be modeled as $P = \frac{\sigma t}{r}$, where σ is the hoop stress.
  - but because σ is a function of ~~extension~~ strain, one pressure can correspond to two stable radii



  - to improve on this, we need a flexible material with a J-shaped stress/strain curve such that stiffness increases significantly on loading

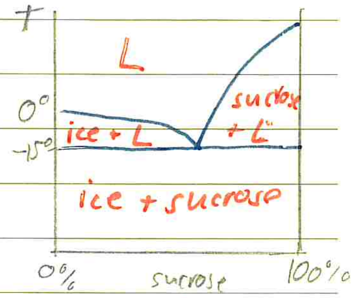


No. 6

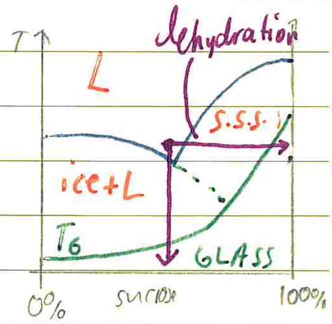
Date 10 . 5 . 19

Phase transformations in living systems

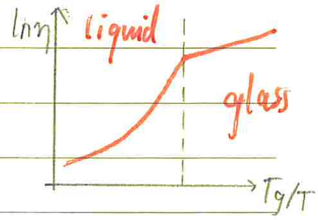
- Animal cells are made of a semi-permeable cell membrane
  - ↳ contains a liquid called cytosol, which can be modeled as a mixture of sugar and water.
  - ↳ formation of crystals in the cytosol is almost always fatal.



- The eq. phase diagram for sucrose-water is eutectic, but there is no solid solubility
  - ↳ i.e ice crystals will be pure.
- We can change the phase by changing the temp. or by hydrating/dehydrating.
- Because crystallisation of sucrose is kinetically difficult, the liquid can be supercooled a lot



- If it is supercooled enough, its viscocity may increase to the point where it can be considered a glass:
  - cutoff is arbitrarily set at $\eta > 10^{12}$ Pa s.
  - the glass transition does not involve structural change or latent heat
  - transition can result from cooling OR dehydration.
  - viscosity as a function of temp. is non-Arrhenius



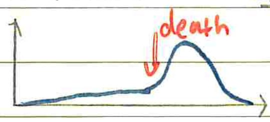
Dehydration in living systems

- When cells dehydrate, their cytosol becomes supersaturated and may crystallise.
- To combat this, some organisms ensure that there are high M_R sugars in the cytosol - more likely to form glasses than crystals
  - ↳ glasses preserve the cell
- This survival mechanism is found in desert plants, and is practically applied to dried foods such as pasta.

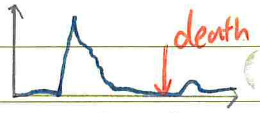
Freezing in living systems

- Because the ice that forms is pure, the cytosol becomes more conc.
  ↳ cell draws in more water by osmosis and may rupture.
- The goal of living systems is to allow for supercooling.
  - bulk water can only be supercooled slightly before freezing.

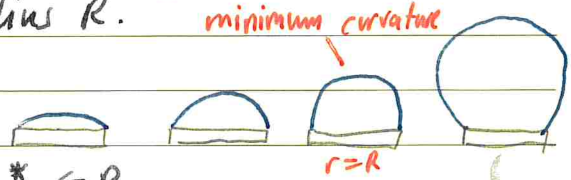
  - in hickory wood, freezing occurs outside the cells first (non-fatal).



  - in peach flower buds, death only occurs when the last 5% of water freezeds



- Freeze avoidance based on subdivision does not work for blood
  ↳ antifreeze proteins bind to growth sites on ice crystals and can thus prevent crystallisation for < 2 K supercooling.
- Some living systems encourage ice formation outside of cells
  ↳ Latent heat released protects the cells, and water diffuses out so the cytosol may form a glass (e.g. Northern Wood frog).
- To do this, intercellular regions contain ice-nucleating agents (INAs).
  - model the INA as a flat disc of radius R.
  - as cap grows, radius of curvature ↓ to min at R, then ↑



  - thus for an ice crystal to grow, $r^* \leq R$

$$r^* = -\frac{2\gamma}{\Delta S \Delta T} \Rightarrow R = \frac{-2\gamma}{\Delta S \Delta T_{crit}} \Rightarrow \boxed{\Delta T_{crit} = \frac{-2\gamma}{\Delta S R}}$$

- Thus to catalyse nucleation for small supercooling, INAs should be as large as possible
  - they are made of proteins that form large flat patches
  - also have a hexagonal pattern with spacings that match the {0001} planes on ice.