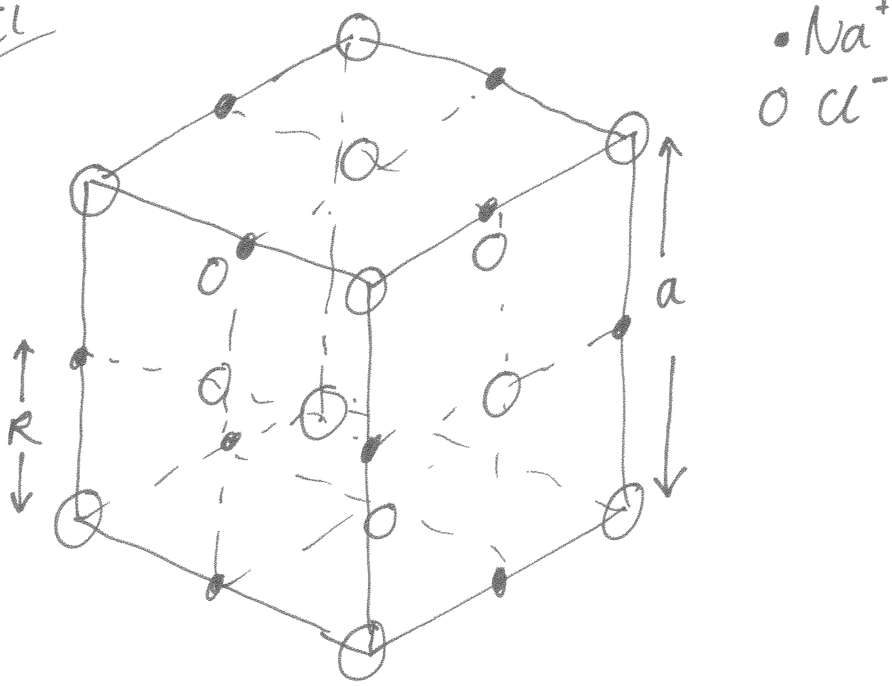
1) a) i) Covalent bonds form when atoms with unfilled electronic shells (or orbitals) share electrons thus giving filled shells and a more stable structure. Typically bond energies in the range of a few eV ($2 \rightarrow 7$ eV) [2]

Bookwork

ii) Hydrogen bonds are polar bonds that form when a hydrogen atom bonded to an electronegative atom such as oxygen or nitrogen interacts with another electronegative atom. Typical bond energy around $0.1 \rightarrow 0.4$ eV (100 meV order) [2]

b) NaCl



[4]

Bookwork

1 c) Consider a Na^+ in the crystal with a charge $+e$.

It has an attractive interaction with 6 nearest neighbours (Cl^-) at a distance R. [2]

It has a repulsive interaction with 12 next-nearest neighbours (Na^+) at a distance $\sqrt{2}R$ [2]

It has an attractive interaction with 8 next-next-nearest neighbours (Cl^-) at a distance $\sqrt{3}R$ [2]

Using electrostatics and adding up the energies

$$U = \frac{-6e^2}{4\pi\varepsilon_r\varepsilon_0 R} + \frac{12e^2}{4\pi\varepsilon_r\varepsilon_0 R\sqrt{2}} - \frac{8e^2}{8\pi\varepsilon_r\varepsilon_0 R\sqrt{3}} + \cdots$$

$$= \frac{-e^2}{4\pi\varepsilon_r\varepsilon_0 R}\Big[\underbrace{6 - 12/\sqrt{2} + 8/\sqrt{3} + \cdots}_{\alpha}\Big]$$

$$= \frac{-\alpha e^2}{4\pi\varepsilon_r\varepsilon_0 R}$$ [2]

1d) i) Chloroform $\varepsilon_r = 4.81$

$$\therefore U = \frac{-1.748 \times (1.6\times10^{-19})^2}{4\pi \times 4.81 \times (8.85\times10^{-12}) \times (0.282\times10^{-9})}$$

$$= -2.97 \times 10^{-19} \text{ J}$$

$$= \frac{-2.97\times10^{-19}}{1.6\times10^{-19}} \text{ eV} = -1.85 \text{ eV}$$ [2]

ii) for water $\varepsilon_r = 80$

$$\therefore U = 1.85 \text{ eV} \times \frac{4.81}{80} = 0.111 \text{ eV}$$ [2]

e) At room temperatu $kT \approx 0.026$ eV

$$\left(\frac{1.38\times10^{-23} \times 300}{1.6\times10^{-19}} = 0.0259 \text{ eV} \right)$$ [1]

In polar liquids are the same or similar order of magnitude to kT becaus of the higher dielectric constant of the liquid, while apolar liquids have much higher cohesive energies $U \gg kT$ becaus of low ε_r values.

This means that bonds in ionic crystals are more easily disrupted by thermal agitation in polar solvents. Hence ionic solids tend to dissolve in them. [4]

2) a) The parameter that controls micelle shape is $H = V/(l_c a_0)$ [2]

i) A spherical micelle occurs if $H \leq 1/3$ [1]

ii) A cylindrical micelle occurs if $1/3 < H \leq 1/2$ [1]

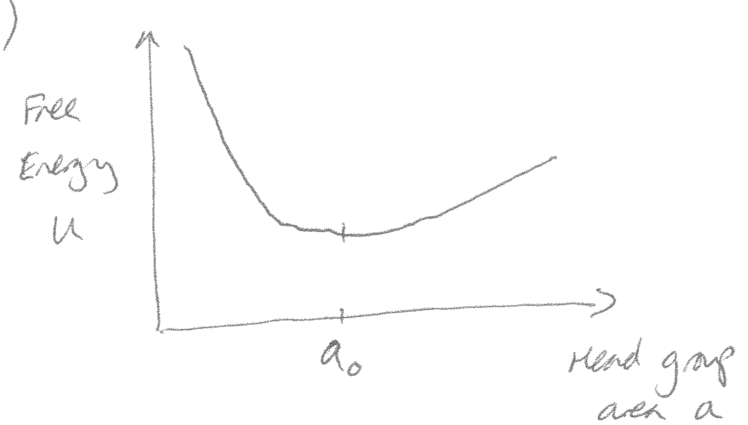
iii) Bilayers require $1/2 < H \leq 1$ [1]

mark for correct numbers & inequalities

~~[1] correctness of~~ $\leq$ ~~rather than~~ $<$ in all examples.

Book work

b) i)



[1] correctly labelled graph

[1] Approx correct shape plot

[1] marking a_0 at minimum

ii) when $a < a_0$ the free energy increases because the charged headgroup of the amphiphiles, which repel each other move closer together [1]

when $a > a_0$ the free energy increases because the increased spacing allows the hydrophobic tails of the amphiphiles to be exposed to water [1]

2c) Taylor expansion: $f(x) \simeq f(x_0) + f'(x_0)(x-x_0) + \frac{1}{2}f''(x_0)(x-x_0)^2 + \ldots$

Expand free energy $U(a)$ where $a = a_0 + \Delta a$ with derivatives performed with respect to a. [1]

$$U(a_0 + \Delta a) \simeq U(a_0) + U'(a_0)(a_0 + \Delta a - a_0) + \frac{1}{2}U''(a_0)(a_0 + \Delta a - a_0)^2$$

$$U(a_0 + \Delta a) \simeq U(a_0) + U'(a_0)\Delta a + \frac{1}{2}U''(a_0)\Delta a^2 + \ldots \text{ [1]}$$

Since $\Delta a << a_0$ ignore higher order terms cubic etc. [1]

We are interested in the change in free energy ΔU

$$\Delta U(\Delta a) = U(a_0 + \Delta a) - U(a_0) \simeq U'(a_0)(\Delta a) + \frac{1}{2}U''(a_0)(\Delta a)^2 \text{ [1]}$$

We know there is a minimum in the free energy so $U'(a_0) = 0$ [1]

$$\Delta U(\Delta a) \simeq \frac{1}{2}U''(a_0)(\Delta a)^2$$

$U''(a_0)$ is a constant which we can write as k [1]

hence

$$\underline{\underline{\Delta U \simeq \frac{1}{2}k\Delta a^2}}$$

d) - Bi-layers undergo thermally induced undulations or modes [1]

- As 2 bi-layers come close together the undulations are sterically restricted due to the presence of the other bi-layer [1]

Bookwork

Either:
- Each mode has $\frac{kT}{2}$ of energy so restricted motion reduces free energy with decreasing distance $\rightarrow$ repulsion [1]

or:

- or: The restricted modes leads to less microstates resulting in decreasing entropy $\rightarrow$ repulsive force [1]

2e) i) Bi-layers will attract when bracket < 0 [1]

Room temp in SI units $T = 293\,K$ [1]

substitution ① $\dfrac{(k_B T)^2}{K\pi^2} = \dfrac{(1.38\times10^{-23} \times 293)^2}{7\times10^{-21}\times\pi^2} = 2.366\times10^{-2}$

② $\dfrac{A}{6\pi} = \dfrac{5\times10^{-21}}{6\pi} = 2.653\times10^{-22}\,J$.

① − ② $= -0.287\times10^{-22}\,J$ [1]

This is < 0 hence attractive.

ii) Begin to repel at T where bracket $= 0$ [1] stated or implied from calc.

Rearrange:

$T = [AK\pi / 6k_B^2]^{0.5}$ [1]

$= [5\times10^{-21} \times 7\times10^{-21} \times \pi / 6 \times (1.38\times10^{-23})^2]^{0.5}$

$T = 310\,K$ or $37\,^\circ C$ [1]

4) a) The electric field of the light is going to induce a dipole moment on the particle given by $p = \alpha E$ where α is the polarisability. [1]

If particle acts like a point dipole [1]

the energy of dipole in the electric field

is $U = -\underline{p}.\underline{E} = -\alpha \underline{E}.\underline{E} = -\alpha E^2$ [1]

Recall that the intensity of the laser beam is related to the electric field by

$$I = \frac{c\varepsilon_0}{2} E^2 \quad \therefore \quad E^2 = \frac{2I}{c\varepsilon_0}$$ [1]

$$\therefore U = -\alpha E^2 = -\frac{\alpha 2I}{c\varepsilon_0} = -\frac{2\alpha}{c\varepsilon_0} I$$ [1]

4 b) If the laser beam has a Gaussian intensity profile

$$I = I_0 \exp\left(\frac{-r^2}{2w_0^2}\right)$$

we can rewrite $\exp(x) = 1 + x + \frac{x^2}{2} +$ higher order terms

but if $r << w_0$ then $\frac{r^2}{w_0^2} << 1$ and higher order terms can be ignored

$$\therefore \quad I \approx I_0\left(1 - \frac{r^2}{2w_0^2}\right)$$

Bookwork

[2]

Force on the particle is

$$F = -\frac{dU}{dx} = \frac{2\alpha}{c\varepsilon_0}\frac{dI}{dx}$$ [1]

$$\frac{dI}{dx} = -\frac{I_0 r}{w_0^2}$$ [1]

$$\therefore F = \frac{-2\alpha I_0 r}{c\varepsilon_0 w_0^2}$$ [1]

This has the form of Hooke's law $F = -kr$ where the effective spring constant

$$k = \frac{2\alpha I_0}{c\varepsilon_0 w_0^2}$$ [1]

4c) If $k = \dfrac{2\alpha I_0}{c\varepsilon_0 \omega_0^2}$ and $\alpha = 4\pi\varepsilon_p\varepsilon_0 R^3$

$$k = \frac{8\pi\varepsilon_p \cancel{\varepsilon_0} R^3 I_0}{\cancel{\varepsilon_0} c\,\omega_0^2} = \frac{8\pi\varepsilon_p R^3 I_0}{c\,\omega_0^2} \quad [1]$$

Laser is focused to a circle with a width i.e. radius of ω_0

$$\therefore I_0 \approx \frac{\text{Power}}{\text{Area}} = \frac{P}{\pi\omega_0^2} \quad [2]$$

$$\therefore k = \frac{8\pi\varepsilon_p R^3 P}{c\,\omega_0^2\,\pi\,\omega_0^2} = \frac{8\varepsilon_p R^3 P}{c\,\omega_0^4} \quad [1]$$

$R = 100\times10^{-9}\,\text{m}$, $P = 1\,\text{W}$, $\omega_0 = 10^{-6}$, $\varepsilon_p = 10$

$$\therefore k = \frac{8\times10\times(100\times10^{-9})\times1}{(3\times10^{8})(10^{-6})^4} = 2.67\times10^{-4}\,\text{Nm}^{-1} \approx 3\times10^{-4}\,\text{Nm}^{-1} \quad [1]$$

4d) If $F = 1\,\text{pN}$, $F = -kr$, $k = 2.67\times10^{-4}\,\text{Nm}^{-1}$

$$\text{Displacement, } r = \frac{F}{k} = \frac{1\times10^{-12}}{2.67\times10^{-4}} = 3.75\times10^{-9}\,\text{m}$$

$$= 3.75\,\text{nm}$$
$$\approx 4\,\text{nm} \quad [3]$$

4) e) If the experiment is conducted in water instead of vacuum

$$k = \frac{8 \varepsilon_p R^3 P}{c w_0^4 \varepsilon_w n_w}$$

$\varepsilon_w = 80 \quad n_w = 1.33$

$$\therefore k = \frac{2.67 \times 10^{-4}}{(80)(1.33)} = 2.5 \times 10^{-6} \ Nm^{-1}$$

$\therefore$ Displacement if $F = 1pN$

$$r = \frac{1 \times 10^{-12}}{2.5 \times 10^{-6}} = 4 \times 10^{-7} m$$

$$= 0.4 \ \mu m.$$ [4]

(Alternatively
$$r_w = r_v \times 80 \times 1.33$$
$$= 3.75 \times 10^{-9} \times 80 \times 1.33$$
$$= 4 \times 10^{-7} m$$
$$= 0.4 \ \mu m$$)

f) Examples include:

- Manipulating glass microspheres in water to make a physical 'Tetris' game, by fast switching of the beams
- Measuring forces between individual DNA molecules tethered to polymer bead held in an optical trap.
- Measuring motor activity of biomolecules by tethering a filament between 2 trapped beads and attaching it to a ~~ar~~ third bea coated with motor proteins. [2]