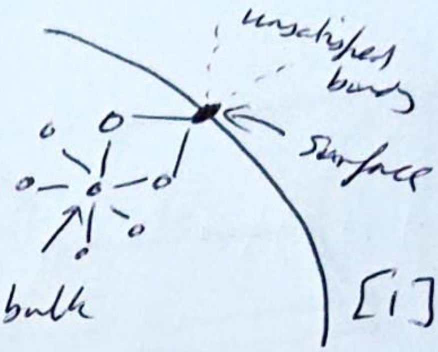
Force & Function

1) a) • Interactions/bonds between neighbouring molecules lower energy of system. [1]

• Each molecule forms bonds/interacts with neighbours [1]



• $N_{bulk} > N_{surface}$. [1]

(6)

• Molecules at surface have unsatisfied bonds [1]

• Energetic cost associated with molecules at surface → interfacial energy [1]

b) • Energetic cost in (a)/interfacial energy proportional to surface area [1]

(2)

• Shape of liquid interface at equilibrium minimises exposed surface area [1]

c) $\Delta P = \gamma \left[\frac{1}{R_1} + \frac{1}{R_2} \right]$ [1]

$R_1 = -R$ [1] for $-$
[½] for R

$R_2 = D/2$ [1/2]

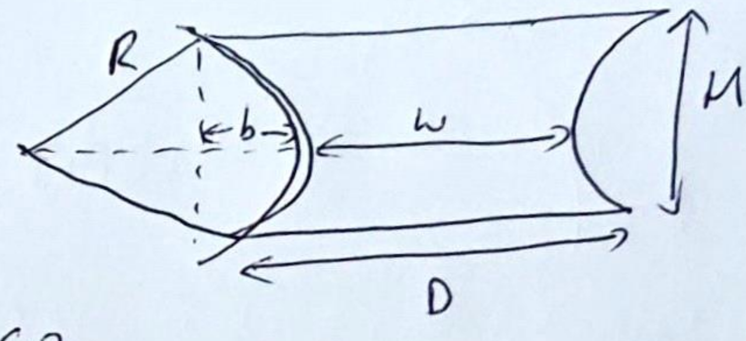
(4)

$\Delta P \simeq -\frac{\gamma}{R}$ [1] $(|R| << D/2)$

1d) $P = \dfrac{-\gamma}{R}$ (allow carry forward for missing − in part c).

$$F = PA = \frac{P\pi D^2}{4} \quad [1]$$

$$F = -\frac{\gamma\pi D^2}{4R} \quad [1]$$



$$R^2 = \left(\frac{H}{2}\right)^2 + (R-b)^2 \quad [1]$$

$$\cancel{R^2} = \frac{H^2}{4} + \cancel{R^2} - 2Rb + b^2 \quad [1]$$

$$R = \frac{H^2}{8b} + \frac{b}{2} \quad [1]$$

7 $$4R = \frac{H^2}{(D-W)} + D - W$$

$$F = \frac{-\gamma\pi D^2}{\frac{H^2}{D-W} + D - W} \quad \text{or} \quad \frac{-\gamma\pi D^2 (D-W)}{H^2 + (D-W)^2} \quad [2]$$

e) $F \simeq -0.113\ \text{N}$ [2]

2

1 for number

1 for unit + sign

No carry forward for sign since should realise from diagram.

f) $P = \gamma\left[\frac{1}{R_1} + \frac{1}{R_2}\right]$

$R_1 = \infty \quad R_2 = D/2$ [1]

$P = \frac{2\gamma}{D}$ [1]

4

$F = \frac{2\pi\gamma D^2/4}{D} = \frac{\gamma\pi D}{2}$ [1]

$F = 0.0057\ N$ [1]

2) a) i) A covalent bond arises from the sharing of a valence electron [1]

The filling of electronic shells creates a stable / energetically favourable structure [1]

ii) $\sim 100\, k_B T$ [1]

b) For an atom to detach it must break free of the covalent bonds [1]

This requires a thermal fluctuation of sufficient energy [1]

~~This~~ The probability of a thermal fluctuation of sufficient energy is controlled by Boltzmann $P \propto e^{-U_B/kT}$ [1]

$P \propto e^{-100}$ is so small as to be negligible / it won't happen. [1]

c) $$U(x) = -\frac{\pi n_1 C}{6}\left(\frac{1}{x^3} - \frac{1}{(x+H)^3}\right)$$

1 atom & film

A single plane of thickness dx in cylinder probe has

$N_2 = n_2 \pi R^2 dx$ atoms [1]

$$U_{plane-film} = -\frac{\pi n_1 C}{6}\left(\frac{1}{x^3} - \frac{1}{(x+H)^3}\right) \times n_2 \pi R^2 dx \quad [1]$$

2c continued.

For whole cylinder integrate [1] limits

$$U_{cylinder\text{-}film} = -\frac{\pi^2 n_1 n_2 C R^2}{6}\int_D^{D+L} \frac{1}{x^3} - \frac{1}{(x+H)^3}\,dx \quad [1]$$

$$U_{cf} = -\frac{AR^2}{6}\left[\frac{-1}{2x^2} + \frac{1}{2(x+H)^2}\right]_D^{D+L} \quad [1]$$

[1] for Hamaker

$$U_{cf} = -\frac{AR^2}{12}\left[\frac{1}{(D+H+L)^2} - \frac{1}{(D+H)^2} - \frac{1}{(D+L)^2} + \frac{1}{D^2}\right]$$

d) if $D \ll L$ some terms insignificant

$$U_{cf} \simeq -\frac{AR^2}{12}\left[\frac{1}{D^2} - \frac{1}{(D+H)^2}\right] \quad [2]$$

e) 1) $$U = -\frac{5\times10^{-20}\times(5\times10^{-6})^2}{12}\left[\frac{1}{(10^{-8})^2} - \frac{1}{(10^{-8}+0.3\times10^{-7})^2}\right]$$

$$= 1.04\times10^{-32}\left[1\times10^{16} - 9.43\times10^{15}\right]$$

$$= 5.93\times10^{-18}\ \text{J} \quad [2]$$

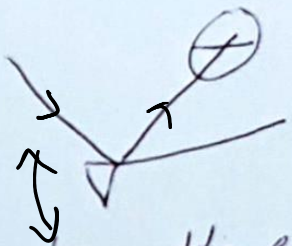
2) if $H \to \infty$ $\frac{1}{D+H} \to 0$ [1]

$$U = 1.04\times10^{-32}\times10^{16} = 1.04\times10^{-16}\ \text{J} \quad [1]$$

f) • when a force interacts with the tip of an AFM this causes the cantilever to bend ~~[illegible]~~ ~~[illegible]~~. [1]

• The deflection is measured using a laser which reflects off back of cantilever onto split photodiode [1]

• Diagram showing deflection of cantilever, laser + PD.



[1]

• If the spring constant of cantilever is known this enables one to measure the force. [1] $F = kz$

• The spring constant can be measured from displacements caused by thermal noise/fluctuations [1]

• $K = \frac{k_B T}{\langle z^2 \rangle}$ [1]

3a) 1) - A colloid in a liquid will undergo Brownian motion [1]
- This results in a random walk [1]

2) $\langle R^2 \rangle \sim 6Dt$
$D = \dfrac{kT}{6\pi\eta a}$ [1]

$\langle R^2 \rangle \sim \dfrac{DTt}{\pi\eta a}$ [1]

$t = \dfrac{4\pi\eta a}{DT\,d^2}$ [1]

3) - The colloid would visit all points in the cavity [1]
- Each point would be visited with equal probability [1]

b) - A microstate is a particular configuration of the particles within the cavity (positions / velocities). [1]
- The entropy is directly related to the number of accessible microstates [1]
- $S = k_B \ln W$. [1]

c) - When the large colloid comes close to wall the small spheres are excluded from the gap. [1]
- However, the total free volume available to microspheres increases. [1]
- Number of microstates increases [1]
- Entropy increases [1]
- $F = +T\dfrac{d\Delta S}{dD}$ $\longrightarrow$ Force attracting big sphere to wall preventing it diffusing round whole cavity [1]

3d) $k = \dfrac{k_B T}{\langle x^2 \rangle}$ [1]

$k = \dfrac{1.38\times10^{-23}\times 290}{5\times10^{-18}}$

$k = 8\times10^{-4}\ \text{Nm}^{-1}$ [1]

3e) $U = -\dfrac{n\pi kT}{3}[a+2r-D]^2[2a+r+D]$

$F = -\dfrac{dU}{dD}$ [1]

$F = +\dfrac{n\pi kT}{3}\dfrac{d}{dD}\underbrace{(a+2r-D)^2}_{x}\underbrace{(2a+r+D)}_{y}$

By product rule $\dfrac{d}{dD} = x\dfrac{dy}{dD} + y\dfrac{dx}{dD}$

$\dfrac{dx}{dD} = -2(a+2r-D)$ [1]

$\dfrac{dy}{dD} = 1$

$F = \dfrac{n\pi kT}{3}\left((a+2r-D)^2 + (2a+r+D)\times-2(a+2r+D)\right)$

$F = \dfrac{n\pi kT}{3}\left((a+2r-D)\left((a+2r-D) - (4a+2r-2D)\right)\right)$ [1]

$F = -\dfrac{n\pi kT}{3}(a+2r-D)(a+D)$ [1]

valid for $a+2r > D$ [1]

3f)

$F_{trap} = F_{Depletion}$ [1]

$\Delta r = \dfrac{F_{Depletion}}{K}$

$F_{Depletion} = -10^{20} \times \pi \times 1.38 \times 10^{-23} \times 290 \times (5\times10^{-6} + 2\times50\times10^{-9} - 5.05\times10^{-6})$
$\times (5\times10^{-6} + 5.05\times10^{-6})$

$F_{depletion} = 0.63\cancel{3}\ pN$ [1]

$\Delta r = \dfrac{6.3\times10^{-13}}{8\times10^{-4}}$ ← from part d

$\Delta r = 0.79\cancel{9}\ nm$ [1]