

1(a) The strength of an interaction is determined by comparison of the magnitude of the potential to $k_B T$ [1]

A weak interaction has a reasonable/negligible probability of
or strong

being disrupted by thermal energy [1]

Some students note $U/kT \sim 100$
or e^{-100} but then later
conclude or values indicate that
they didn't realize how this related
to strength of
bond in kT .

$$\text{Probability} \propto \exp(-U/kT) [1]$$

Covalent bond $\sim 100 kT$

(50 - 250)

[1/2]

Vdw

$\sim 2 kT$

(1 - 5)

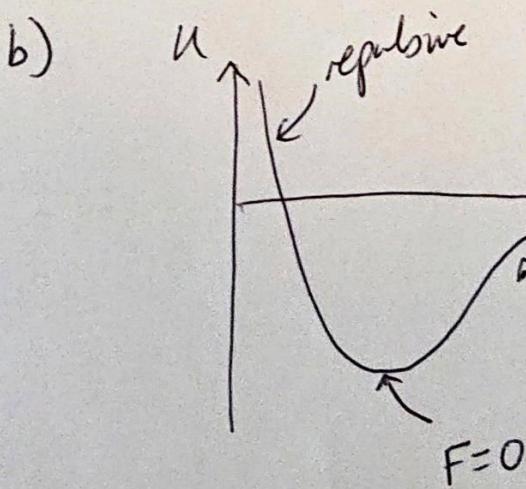
[1/2]

$$e^{-U/kT} = e^{-100}$$

$$P_{\text{covalent}} \propto e^{-100}$$

$$P_{\text{vdw}} \propto e^{-2}$$

Vdw interaction much more likely
to be disrupted by thermal energy than
covalent [1] (5)



Pauli [repulsive]

curve shape [1]

repulsive/attractive [1]

$F=0$ [1]

Some ambiguity in q.
accepted either "attractive contribution"
{, potential or region that is
attractive.

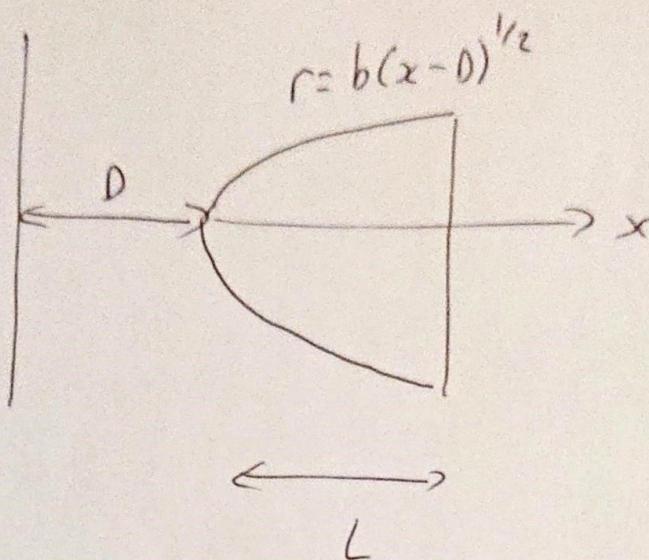
Pauli exclusion principle creates a strong repulsion as orbitals overlap [1] → can state PEP as alternative.

Dispersion Interaction (attractive)

- 1) Temporary fluctuations in charge density create an instantaneous dipole [1]
- 2) Resulting electric field produces induced dipole in neighbor [1]
- 3) The dipoles attract electrostatically. [1]

(7)

c)



split up shape into thin circular discs. No atoms/slice is

$$N_2 = n_2 \pi r^2 dx \quad [1]$$

↗
no. density

$$du_{disk} = -\frac{\pi n_1 C}{6x^3} n_2 \pi r^2 dx \quad [1]$$

$$A = \pi^2 n_1 n_2 C \quad \text{"Hausker const"} \quad [1]$$

$$du = -\frac{Ab^2}{6} \frac{dx - D}{x^3} \quad [1]$$

$$u_{tot} = \int_D^{D+L} -\frac{Ab^2}{6} \left(\frac{1}{x^2} - \frac{D}{x^3} \right) dx \quad [1] \quad \text{correct (units)}$$

$$= -\frac{Ab^2}{6} \left[-\frac{1}{x} + \frac{D}{2x^2} \right]_D^{D+L} \quad [1] \quad \text{correct integration}$$

~~$$= -\frac{Ab^2}{6} \left[\frac{1}{D+L} + \frac{1}{D} + \frac{D}{(D+L)^2} - \frac{2D}{D^2} \right]$$~~

Substitution

$$-\frac{Ab^2}{6} \left[-\frac{1}{x} + \frac{D}{2x^2} \right]_0^{D+L}$$

$$-\frac{Ab^2}{6} \left[-\frac{1}{D+L} + \frac{1}{D} + \frac{D}{2(D+L)^2} - \frac{D}{2D^2} \right] [1] \text{ substitution}$$

$$-\frac{Ab^2}{6} \left[\frac{-1}{(D+L)} + \frac{1}{2D} + \frac{D}{2(D+L)^2} \right]$$

$$-\frac{Ab^2}{6} \left[\frac{-2D + D+L}{2D(D+L)} + \frac{D}{2(D+L)^2} \right]$$

$$-\frac{Ab^2}{6} \left[\frac{L - D}{2D(D+L)} + \frac{D}{2(D+L)^2} \right]$$

$$-\frac{Ab^2}{6} \left[\frac{(L - D)(D+L)}{2D(D+L)^2} + \frac{D^2}{2D(D+L)^2} \right]$$

$$-\frac{Ab^2}{6} \left[\frac{L^2 - D^2 + D^2}{2D(D+L)^2} \right]$$

$$M_{tot} = -\frac{Ab^2}{6} \left[\frac{L^2}{2D(D+L)^2} \right] [2]$$

108 if not simplified

9

$$d) \frac{1}{2} k_B T = \frac{1}{2} k \langle \Delta z^2 \rangle \quad [1]$$

$$k \triangleq \frac{k_B T}{\langle \Delta z^2 \rangle} \quad [2]$$

$$F = k \Delta z = \frac{k_B T}{\langle \Delta z^2 \rangle} \times \Delta z \quad [1]$$

$$\Delta z = \frac{F \langle \Delta z^2 \rangle}{k_B T} = \quad [1]$$

$$\Delta z = \frac{10 \times 10^{-9} \times 1 \times 10^{-24}}{1.38 \times 10^{-23} \times 300}$$

$$\Delta z = \underline{\underline{2.4 \text{ nm}}} \quad [1] \quad \textcircled{4}$$

- 2a) • within a liquid atoms/molecules undergo favourable interactions with neighbouring atoms/molecules [1]
- Total interaction \sim strength of interaction^(a) multiplied by no. nearest neighbours N ie $U_{tot} = -N U_{\text{single}}$ [1]
 - Atoms/molecules in bulk have more nearest neighbours than those at surface [1]
 - This leads to an energetic cost associated with the area of the interface [1]
 - Area n droplets is minimised by forming 1 large droplet [1]
- (5)

- b)
- Amphiphiles consist of hydrophobic tails & hydrophilic headgroups [1]
 - Amphiphiles sit at interface between water + oil reduces removing cost of interface [1] contact area $\frac{1}{2}$
 - Hence no change in free energy or driving force to cause droplets to coalesce [1]

(3)

2c)

Pressure drop across curved interface balances weight of fluid. [1]

$$\Delta p = \frac{mg}{a} = \rho gh$$

$$r_1 = r_2 \Rightarrow \Delta p = \frac{2\gamma}{r} [1]$$

$$\frac{2\gamma}{r} = \rho gh \Rightarrow h = \frac{2\gamma}{\rho gr} [1]$$

$$h = \frac{2 \times 72 \times 10^{-3}}{1000 \times 9.81 \times 10^{-5}} = 1.46 \text{ m} [1]$$

$h \ll 5 \text{ m}$ hence explanation unreasonable [1]

(5)

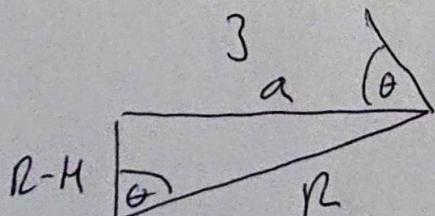
d)

Balancing horizontal forces on contact line

$$\gamma_{WA} \cos\theta + \gamma_{LW} = \gamma_{LA} [1]$$

$$\cos\theta = \frac{46 - 10}{72} = 0.5 [1]$$

$$V = \frac{\pi h^2}{3} (3R - h)$$



$$\cos\theta = \frac{R-h}{R}$$

$$\text{hence } h = R(1 - \cos\theta) [1]$$

$$V = \frac{\pi R^3}{3} \underbrace{(1-\cos\theta)^2}_{h^2} \left(3R - \underbrace{R(1-\cos\theta)}_h \right) \quad [1]$$

$$V = \frac{\pi R^3}{3} (1-\cos\theta)^2 (2+\cos\theta)$$

$$R = \left(\frac{3V}{\pi(1-\cos\theta)^2(2+\cos\theta)} \right)^{1/3} \quad [1]$$

Basal area $A = \pi a^2 \quad [1]$

$$(R-h)^2 + a^2 = R^2 \quad \text{pythagoras}$$

$$a^2 = R^2 - (R-h)^2 \\ = R^2 - (R-R(1-\cos\theta))^2$$

$$a^2 = R^2(1-\cos^2\theta) \quad [1]$$

$$A = \pi \left(\frac{3V}{\pi(1-\cos\theta)^2(2+\cos\theta)} \right)^{2/3} (1-\cos^2\theta) \quad [1]$$

$$= \pi \left(\frac{3 \times 1}{\pi(1-0.5)^2(2+0.5)} \right)^{2/3} (1-0.5^2)$$

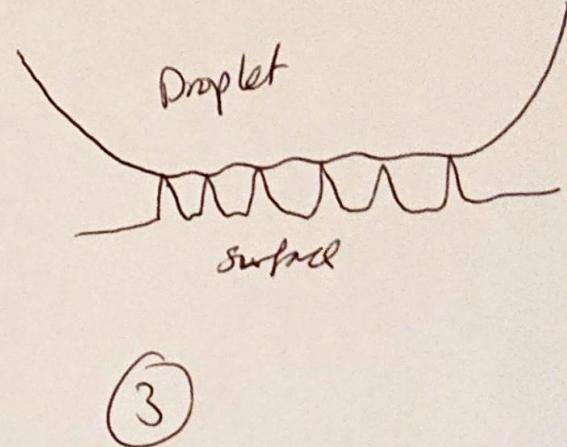
$$A \approx 3.1 \text{ mm}^2 \quad [1]$$

There are other ways to solve this. Divide marks as shown.

⑨

- 2e) Lotus leaf / superhydrophobic surfaces have a lot of small spikes / pillars [1]
- As a result droplet contact area is much smaller [1]

A droplet in air forms a sphere to minimise exposed surface area.
Similar shape on leaf because most interface is water-air. [1]



3a)

- No. of microstates is proportional to available volume for ions.
(which are held in gap by electric field.) [1]

- As plates move apart & water enters gap no. microstates increases [1]

$$S = k_B \ln \Omega \quad [1]$$

↗ ↗
Entropy microstates

These can be described in words

$$\Delta F_{\text{free energy}} = \cancel{\Delta H} - TAS \quad [1]$$

$\cancel{\Delta H}$ ↙
no enthalpy change.

The free energy decreases with increasing entropy.

$$\text{free} = - \frac{dF}{dD} = \frac{TdS}{dD} \quad [1]$$

force related to change of entropy with plate separation

$$\Delta S = k_B [\ln \Omega_{\text{far apart}} - \ln \Omega_{\text{close}}] > 0 \quad [1]$$

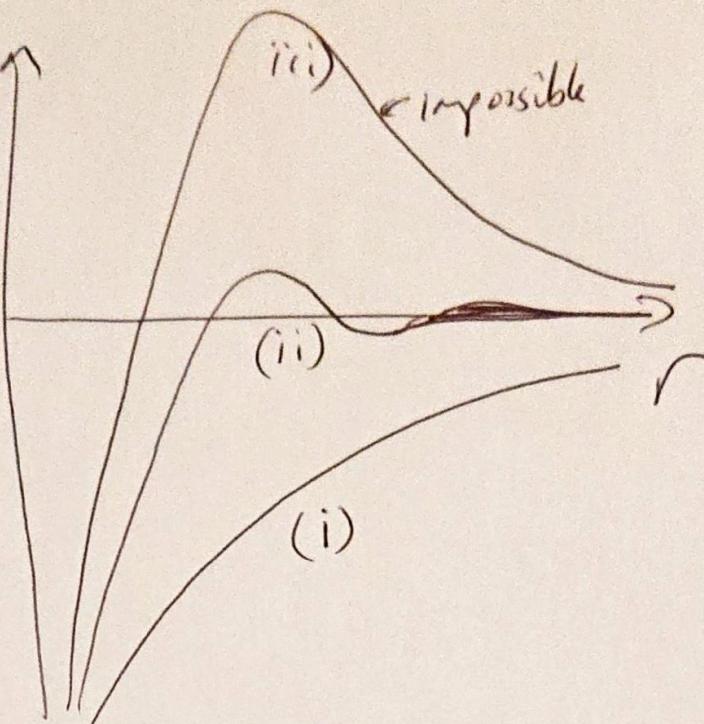
"increase in entropy due to increased no. microstates"

$$\text{so force} > 0 \quad [1]$$

hence repulsive.

(7)

3b)



[1] labels

[1] impossible

[1] weak must show 2nd min

[1] strong

- i) strongly attractive at all r . once particles stick they trapped in primary minimum & can't escape due to thermal fluctuations [1]
- ii) Potential has a weak secondary minimum. Particles get stuck (aggregate) but thermal fluctuations are enough to break particles apart [1]
- iii) Potential has large repulsive energy barrier which makes it impossible for particles to come together [1]

⑦

$$3c) \frac{du}{dN} = -N_B + \frac{8\pi\gamma}{3N^{1/3}} \left(\frac{3V}{4\pi} \right)^{2/3}$$

when $N = N_c$ $\frac{du}{dN} = 0$ [1]

$$N_B = \frac{8\pi\gamma}{3N_c^{1/3}} \left(\frac{3V}{4\pi} \right)^{2/3}$$

$$N_c = \left(\frac{8\pi\gamma}{3N_B} \right)^3 \left(\frac{3V}{4\pi} \right)^2 [1]$$

$$N_c = \left(\frac{8\pi \times 1.5 \times 10^{-3}}{3 \times 10^{-23} \times 1.38 \times 10^{-23} \times 300} \right)^3 \left(\frac{3 \times 125 \times 10^{-27}}{4\pi} \right)^2$$

[1] for correct units conversion

$$N_c \approx 24.8 [1]$$

$$N_c \approx 25 [1]$$

1 for correct numerical result but extra 1 since must have whole number molecules.

3d) - In order for an aggregate to form you need a thermal fluctuation to overcome the energy barrier to nucleation [1] energy barrier

- Probability $\propto \exp(-U/kT)$ [1]
- hence takes time if probability is low to get a fluctuation by chance. [1]
- Probability increases dramatically if you increase temperature in practice when sample is cold probability is too low to happen on sensible timescale [1]
- Aggregates forming on spoon / edge / surface are undergoing heterogeneous nucleation. [1]
- The surface reduces the critical nucleus size & hence the energy barrier is smaller. This leads to faster nucleation [1]

(6)