at the same two temperatures.
According to the Debye model the root-mean-square displacement of Pt is given by

$$\langle u^2 \rangle^{1/2} = \sqrt{\frac{3 N_A \hbar^2 T}{M k_B \theta_D^2}} = 3.815 \times 10^{-11} \text{ m kg}^{1/2} \text{ K}^{1/2} \sqrt{\frac{T}{M \theta_D^2}} = 0.3815 \text{ Å kg}^{1/2} \text{ K}^{1/2} \sqrt{\frac{T}{M \theta_D^2}}$$

with $M = 0.19508$ kg mol^{-1} and $\Theta_D = 240$ K.

Thus $\langle u^2 \rangle^{1/2}|_{300 K} = 0.0623$ Å and $\langle u^2 \rangle^{1/2}|_{2045 K} = 0.163$ Å.

For the fractional displacement we need to calculate the equilibrium Pt–Pt distance. Since Pt is an fcc metal, the nearest neighbour distance is given by $a/\sqrt{2}$ (where a is the lattice constant) $= 3.92$ Å$/\sqrt{2} = 2.77$ Å. Therefore,

$$\frac{\langle u^2 \rangle^{1/2}|_{300 K}}{2.77 \text{ Å}} = 0.0225 \text{ and } \frac{\langle u^2 \rangle^{1/2}|_{2045 K}}{2.77 \text{ Å}} = 0.0588.$$

(a) For diamond $M = 0.0120$ kg mol^{-1} and $\theta_D = 2230$ K.

Thus $\langle u^2 \rangle^{1/2}|_{300 K} = 0.0271$ Å and $\langle u^2 \rangle^{1/2}|_{2045 K} = 0.0706$ Å.

The absolute motion of a C(diamond) atom at these temperatures corresponds to only about 43% of that of a Pt atom.

1.14 The surface Debye temperature of Pt(100) is 110 K. Take the definition of melting to be the point at which the fractional displacement relative to the lattice constant is equal to ~ 8.3% (Lindemann criterion). What is the surface melting temperature of Pt(100)? What is the implication of a surface that melts at a lower temperature than the bulk?

Solving the root mean square displacement equation, Eq. (1.8.6), for T yields

$$T_f = M \theta_D^2 (0.083 x/c)^2$$

where $x = \sqrt{2}a$ is the nearest neighbour distance and $c = 0.3815$ Å kg$^{-1/2}$ K$^{-1/2}$. The surface melting temperature is found by substituting $\theta_s = 110$ K for θ_D and $x = 2.77$ Å. T_f(surface) = 857 K, significantly below the bulk melting point of 2045 K.

A liquid layer covers the bulk solid. The layer grows in thickness as each successively deeper solid layer becomes the surface layer of the solid. Thus melting starts at the surface and proceeds back into the bulk.

1.15 The bulk terminated Si(100)–(1 × 1) surface has two dangling bonds per surface atom and is, therefore, unstable toward reconstruction. Approximate the dangling bonds as effectively being half-filled sp^3 orbitals. The driving force of reconstruction is the removal of dangling bonds. (a) The stable room temperature surface reconstructs into a (2 × 1) unit cell in which the surface atoms move closer to each other in one direction but the distance is not changed in the perpendicular direction. Discuss how the loss of one dangling bond on each Si atom leads to the formation of a (2 × 1) unit cell. Hint: The nearest neighbour surface Si atoms are called dimers. (b) This leaves one dangling bond per surface atom. Describe the nature of the interaction of these dangling

bonds that leads to (i) symmetric dimers and (ii) ... d adsorption on the symmetry of these two types of dimers. F... sp^3 orbitals can make. Second, two equivalent dangling b... states.

There are two ways in which the sp^3 like dangling bon... tion. This leads to symmetric dimers as one would expec... interaction and the equivalence of the two bonding orbita... tem is unstable with respect to a Jahn-Teller distortion un... Jahn-Teller effect. Therefore, the system will spontaneous... in the lower energy state than in the higher energy state.... This leads to a splitting of the electronic states into two sta... H atom adsorption breaks the π bond and negates th... which interaction was first present, the structure of the d... same in either case. It is unclear whether this should be sy... but it will be less symmetric than a dimer with two H ato... with no H atoms adsorbed. A dimer with two adsorbed H...

1.16 Describe the features a, b, c, and d in Fig. 1.19.
(a) is an occupied surface resonance. It is a resonance... projected bulk band structure, i.e. it overlaps bulk ban...
(b) is an occupied surface state. It is a surface state beca... region where bulk states are forbidden). Both a and...
(c) is a normally unoccupied surface state. Both c...
(d) is a normally unoccupied surface resonance. Both... they lie above E_F.

1.17 What is the significance of a band gap? (b) What differentia...
(a) A band gap is a region of k space in which no bul... states can have the combination of energy and mom... that lies in a band gap will be weakly coupled to bul... band edge, the more weakly it will be coupled (all ot... The presence and size of a band gap also determines... semiconductor or insulator.
(b) A partial band gap is a small region of k space in whi... A full band gap exists in a certain energy range for a...

1.18 What are E_g, E_F, E_C, E_V and E_{vac}? (b)...
E_g is the magnitude of the band gap. A band gap can be... difference in a diagram such as Fig. 1.19) or indirect (the... between points with different values of k.
E_F is the Fermi energy. It is the highest allowed en... perfect intrinsic (undoped) semiconductor, there are no ... band gap.
E_C is the conduction band minimum, the lowest energ...
E_V is the valence band maximum, the highest energy

$$\times 10^{-11}\ \text{m kg}^{1/2}\ \text{K}^{1/2}\ \sqrt{\frac{T}{M\theta_D^2}} = 0.3815\ \text{Å kg}^{1/2}\ \text{K}^{1/2}\ \sqrt{\frac{T}{M\theta_D^2}}$$

$\Theta_D = 240$ K.

n-square displacement of the C atoms at the surface of diamond

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direction but the distance is not changed in the perpendicular

one dangling bond on each Si atom leads to the formation

earest neighbour surface Si atoms are called dimers. (b) This

ce atom. Describe the nature of the interaction of these dangling

bonds that leads to (i) symmetric dimers and (ii) tilted dimers. (c) Predict the effect of hydrogen adsorption on the symmetry of these two types of dimers. Hint: Consider first the types of bonds that sp^3 orbitals can make. Second, two equivalent dangling bonds represent two degenerate electronic states.

There are two ways in which the sp^3 like dangling bond orbitals can interact. (a) π bond forma-tion. This leads to symmetric dimers as one would expect based on the symmetry of the bonding interaction and the equivalence of the two bonding orbitals. (b) The two dangling bonds represent two degenerate half-filled electronic states when they are in a symmetric configuration. Such a sys-tem is unstable with respect to a Jahn-Teller distortion unless some other interaction overrides the Jahn-Teller effect. Therefore, the system will spontaneously break symmetry by tilting the dimer. This leads to a splitting of the electronic states into two states, with a higher population of electrons in the lower energy state than in the higher energy state.

H atom adsorption breaks the π bond and negates the Jahn-Teller effect. Thus, regardless of which interaction was first present, the structure of the dimer with one H atom on it will be the same in either case. It is unclear whether this should be symmetric or not based on simple arguments but it will be less symmetric than a dimer with two H atoms adsorbed and less tilted than a dimer with no H atoms adsorbed. A dimer with two adsorbed H atoms will be symmetric.

1.16 Describe the features a, b, c, and d in Fig. 1.19.

(a) is an occupied surface resonance. It is a resonance since it falls in an allowed part of the projected bulk band structure, i.e. it overlaps bulk bands.

(b) is an occupied surface state. It is a surface state because it appears in part of the band gap (a region where bulk states are forbidden). Both a and b are occupied because they are located below the Fermi energy, E_F.

(c) is a normally unoccupied surface state.

(d) is a normally unoccupied surface resonance. Both c and d are normally unoccupied because they lie above E_F.

1.17 What is the significance of a band gap? (b) What differentiates a partial band gap from a full band gap?

(a) A band gap is a region of k space in which no bulk bands exist. Only defect states or surface states can have the combination of energy and momentum that lies in a band gap. Any state that lies in a band gap will be weakly coupled to bulk states and the farther away it is from a band edge, the more weakly it will be coupled (all other things such as symmetry being equal). The presence and size of a band gap also determines whether a material is a metal, semimetal, semiconductor or insulator.

(b) A partial band gap is a small region of k space in which states of a given energy are not allowed. A full band gap exists in a certain energy range for all values of crystal momentum.

1.18 What are E_g, E_F, E_C, E_V and E_{vac} as shown, for instance, in Fig. 1.19?

E_g is the magnitude of the band gap. A band gap can be either direct (the minimum vertical energy difference in a diagram such as Fig. 1.19) or indirect (the minimum energy difference, which occurs between points with different values of **k**).

E_F is the Fermi energy. It is the highest allowed energy for electrons at 0 K. However, in a perfect intrinsic (undoped) semiconductor, there are no states at E_F because it lies midway in the band gap.

E_C is the conduction band minimum, the lowest energy point in the conduction band.
E_V is the valence band maximum, the highest energy point in the valence band.

2.13 Fractional coverage can be defined as the number of adsorbates divided by the number of surface atoms:

$$\theta = N_{ads} / N_0.$$

(2.12.3)

For each of the structures in Exercise 2.12, calculate the coverage. Note any correlations between coverage and the LEED patterns.

The area of a unit cell is proportional to the product of the unit vectors that describe the unit cell. The coverage is given by the number of adsorbates per unit cell, n_{unit}, divided by the area of the substrate unit cell, divided by the area of the substrate unit cell. In Wood's notation the unit cell adsorbate unit cell, divided by the area of the substrate unit cell. In Wood's notation the unit cell has a (1×1) dimension and an area of 1 unit. Thus the fractional coverage is simply

$$\theta = n_{unit}/(nm) = 1/\det M$$

where n and m are the indicies used in Wood's notation. Obviously, this relationship only holds if Wood's notation can be used to describe the structure. It must also be kept in mind that an ordered array of vacancies gives the same diffraction pattern as the analogous ordered array of filled sites.

(a) $\theta = 1/12\,ML$. (b) $\theta = 0.25\,ML$. (c) $\theta = 0.5\,ML$. (d) $\theta = 0.25\,ML$. (e) $\theta = 0.25\,ML$. (f) $\theta = 0.5\,ML$. (g) $\theta = 0.33\,ML$. (h) $\theta = 0.5\,ML$. (i) $\theta = 0.25\,ML$.

2.14 Given LEED patterns (a)–(g) in Fig. 2.30 obtained from adsorbate-covered face-centred cubic (fcc) substrates, determine the surface structures. Substrate reflexes are marked while the additional adsorbate induced reflexes are marked ×. Assume no reconstruction of the surface.

(a) $\mathbf{M}^* = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix}$.

$$\mathbf{M} = \frac{1}{\frac{1}{4} + \frac{1}{4}} \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}.$$

$\theta = 0.5\,ML$. In Wood's notation c(2×2) or p$\left(\sqrt{2} \times \sqrt{2}\right)$ R45°.

Figure Exercise 2.14(a) *Real space and reciprocal space depictions of a c2×2p $\left(\sqrt{2} \times \sqrt{2}\right)$ R45° structure.*

(b) $\mathbf{M}^* = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$.

$$\mathbf{M} = \frac{1}{\frac{1}{4}} \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}.$$

The p(2×2) structure can either correspond to vacancies, that is, $\frac{3}{4}\,ML$ of ordered filled sites. O problem of relating a diffraction pattern, which unique.
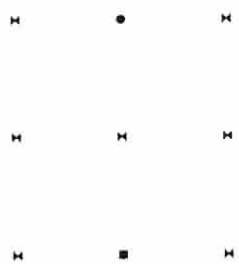
Figure Exercise 2.14(b) *Real space and reciproca*

(c) $\mathbf{M}^* = \begin{pmatrix} \frac{1}{4} & -\frac{1}{2} \\ \frac{1}{4} & \frac{1}{2} \end{pmatrix}$.

$$\mathbf{M} = \frac{1}{\frac{1}{4}} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ -\frac{1}{4} & \frac{1}{4} \end{pmatrix} = \begin{pmatrix} 2 & -1 \\ 2 & 1 \end{pmatrix}.$$
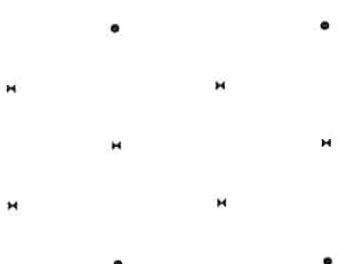
Figure Exercise 2.14(c) *Real space and reciproc*

fined as the number of adsorbates divided by the number of surface

$$\theta = N_{ads} / N_0.$$

xercise 2.12, calculate the coverage. Note any correlations between ns.

portional to the product of the unit vectors that describe the unit cell, number of adsorbates per unit cell, n_{unit}, divided by the area of the the area of the substrate unit cell. In Wood's notation the unit cell area of 1 unit. Thus the fractional coverage is simply

$$\theta = n_{unit}/(nm) = 1/\det M$$

used in Wood's notation. Obviously, this relationship only holds d to describe the structure. It must also be kept in mind that an s the same diffraction pattern as the analogous ordered array of

25 ML. (c) $\theta = 0.5$ ML. (d) $\theta = 0.25$ ML. (e) $\theta = 0.25$ ML.
L. (h) $\theta = 0.5$ ML. (i) $\theta = 0.25$ ML.
n Fig. 2.30 obtained from adsorbate-covered face-centred cubic
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$$\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}.$$

otation c(2 × 2) or p$\left(\sqrt{2} \times \sqrt{2}\right)$ R45°.

(b) $M^* = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}.$

$M = \frac{1}{\frac{1}{4}}\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}.$

The p(2 × 2) structure can either correspond to $\frac{1}{4}$ ML of ordered vacancies, that is, $\frac{3}{4}$ ML of ordered filled sites or $\frac{1}{4}$ ML of ordered filled sites. Care must be taken when performing the inverse problem of relating a diffraction pattern, which is not unique, to a real space structure, which is unique.

(c) $M^* = \begin{pmatrix} \frac{1}{4} & -\frac{1}{2} \\ \frac{1}{4} & \frac{1}{2} \end{pmatrix}.$

$M = \frac{1}{\frac{1}{4}}\begin{pmatrix} \frac{1}{2} & -\frac{1}{4} \\ \frac{1}{2} & \frac{1}{4} \end{pmatrix} = \begin{pmatrix} 2 & -1 \\ 2 & 1 \end{pmatrix}.$
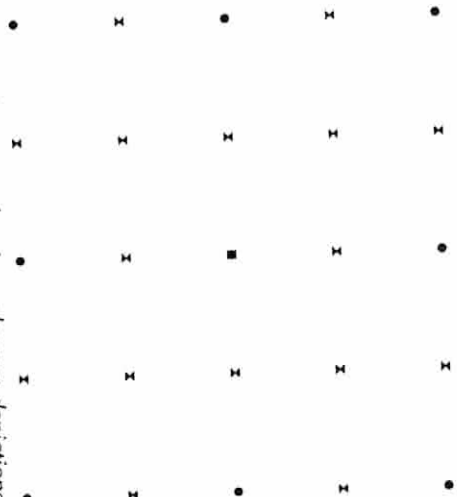
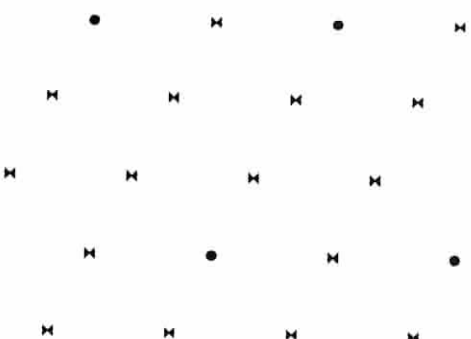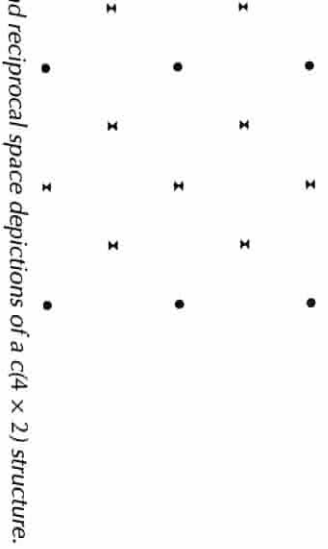**Figure Exercise 2.14(b)**   Real space and reciprocal space depictions of a c(2 × 2) structure.
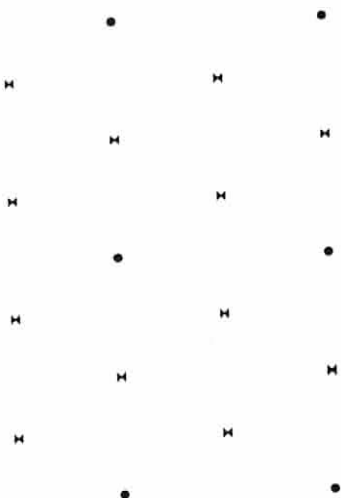
The c(4 × 2) structure can either correspond to $\frac{1}{4}$ ML of ordered filled sites or $\frac{1}{4}$ ML of ordered vacancies, that is, $\frac{3}{4}$ ML of ordered filled sites.

(d) $M^* = \begin{pmatrix} \frac{1}{4} & -\frac{1}{2} \\ \frac{1}{4} & \frac{1}{4} \end{pmatrix}$.

   $M = \frac{1}{\frac{1}{4}}\begin{pmatrix} \frac{1}{2} & -\frac{1}{4} \\ \frac{1}{2} & \frac{1}{4} \end{pmatrix} = \begin{pmatrix} 2 & -1 \\ 2 & 1 \end{pmatrix}$

This apparent c(4 × 2) structure can either correspond to $\frac{1}{4}$ ML of ordered filled sites or $\frac{1}{4}$ ML of ordered vacancies, that is, $\frac{3}{4}$ ML of ordered filled sites. The choice of site is arbitrary as the pattern cannot differentiate between long bridge, short bridge or on-top site. However, contrary to the square lattice (100), c(4 × 2) on the square lattice (100), c(4 × 2) can be distinguished from c(2 × 4) because of the rectangular lattice on (110).
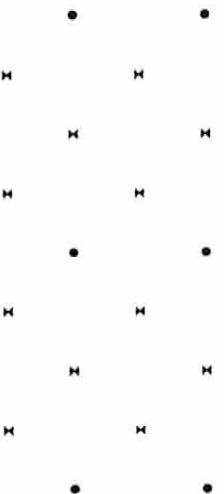
Figure Exercise 2.14(d) Real space and reciprocal space depictions of a c(4 × 2) structure.

(e) $M^* = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$.

   $M = \frac{1}{\frac{1}{2}}\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$.

The p(1 × 2) structure, 0.5 ML.
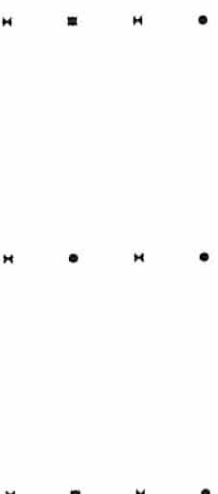
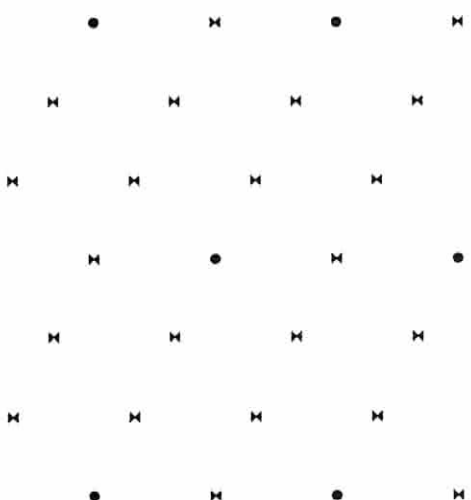**Figure Exercise 2.14(e)**   Real space and reciprocal space depictions of a c(4 × 2) structure.

(f) $M^* = \begin{pmatrix} \frac{1}{3} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$.

   $M = \frac{1}{\frac{1}{6}}\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{3} \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 0 & 2 \end{pmatrix}$.

The p(3 × 2) structure shown with $\theta = 1/6$ ML.

Figure Exercise 2.14(f)   Real space and reciprocal spa

(g) $M^* = \begin{pmatrix} \frac{1}{3} & 0 \\ 0 & 1 \end{pmatrix}$.

   $M = \frac{1}{\frac{1}{3}}\begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{3} \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}$.

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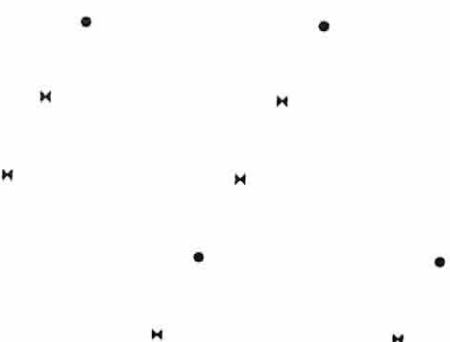
correspond to $\frac{1}{4}$ ML of ordered filled sites or $\frac{1}{4}$ ML of ordered filled sites.

an either correspond to $\frac{1}{4}$ ML of ordered filled sites or $\frac{1}{4}$ ML of ordered filled sites. The choice of site is arbitrary as the long bridge, short bridge or on-top site. However, contrary (100), c(4 × 2) can be distinguished from c(2 × 4) because
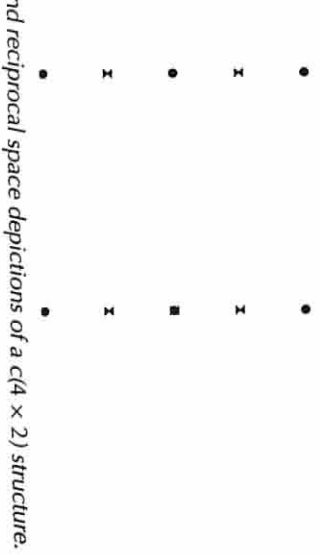
d reciprocal space depictions of a c(4 × 2) structure.

nd reciprocal space depictions of a c(4 × 2) structure.

(f) $M^* = \begin{pmatrix} \frac{1}{3} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$.

$M = \frac{1}{6}\begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{3} \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 0 & 2 \end{pmatrix}$.

The p(3 × 2) structure shown with $\theta = 1/6$ ML as opposed to the $\theta = 5/6$ ML structure.

Figure Exercise 2.14(f) Real space and reciprocal space depictions of a p(3 × 2) structure.

(g) $M^* = \begin{pmatrix} \frac{1}{3} & 0 \\ 0 & 1 \end{pmatrix}$.

$M = \frac{1}{3}\begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{3} \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 0 & 1 \end{pmatrix}$.
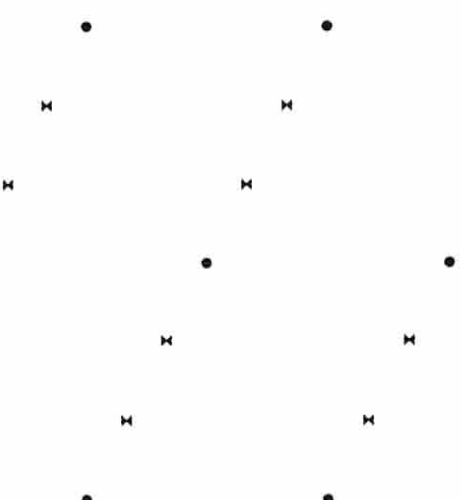
ven by

$$= \frac{1}{A} \exp\left(E_{des}/RT\right)$$

face due to diffusion, d, is given by

$$= [x^2]^{1/2} = (4D\tau)^{1/2}$$

$$(E_d/RT) \times 4D_0 \exp(-E_{dif}/RT)$$
$$\text{xp}\left(\frac{E_{des} - E_{dif}}{RT}\right)\Big)\Big]^{1/2}$$

surfaces, it changes its orientation as a function of coverage.
ridine can experience and how this affects the orientation

es can involve either the system of π electrons parallel to
rs to lie flat on a metal surface, or it can involve the lone
onding through the lone pair will lead to the N end being
end points away. A transition from one type to the other
g down geometry requires more space than the standing
olecules on the surface, i.e. with increasing coverage, the
room for the added molecules.

age has been observed on Ag(111), Ni(100), and Pt(110).
is seen on Pd(111). Tilted pyridine has been observed on

weakly on Ag(111). Given that the double bond in C_5H_8
wn in the figure below, suggest a configuration for the
ped Ag surface with (111) terraces.
pole-dipole interaction between the molecule and a step
adsorbate geometry. The lowest energy configuration is
. Thus the top of the pentagon will point in the downstairs
the top of the step.
higher co-ordination number (on-top → two-fold bridge
, both the π and σ contributions to bonding increase in
n the CO stretching frequency and chemisorption bond

the surface is weak, which adsorption site is preferred?
occurs via charge donation from the 5σ orbital and
* antibonding orbital. The occupied 1π orbital is also
system with the metal. The interaction of the σ orbitals
lesser extent) is more or less non-bonding (perhaps even
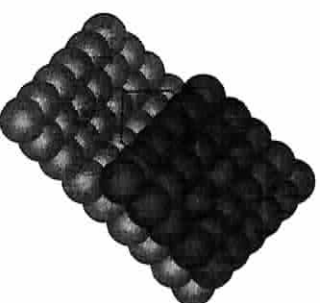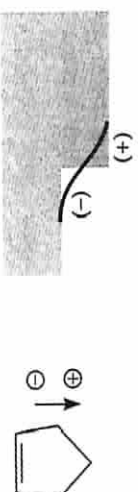e π system are primarily responsible for the metal –CO

3.6

Figure Exercise 3.4 *Schematic drawing of cyclopentene adsorbed on a stepped Ag surface.*

chemisorption bond. This back-donation weakens the $C\equiv O$ bond. At higher coordination, there is an increased back-donation of charge from more than one atom. As a result, the $C\equiv O$ bond becomes weaker and the force constant decreases accordingly. Thus the ν_{CO} stretching frequency shifts to lower wavenumbers. It is generally accepted that $\nu_{CO} \approx 2000$ cm^{-1} corresponds to linear bonding, $1850 \leq \tilde{\nu} \leq 2000$ cm^{-1} indicates bridge bonding (two-fold symmetry) and higher co-ordination can be assigned to frequencies below 1850 cm^{-1}.

In adsorption systems where the π interaction is weaker, such as CO on Cu or N_2 on Ni(100), the σ repulsion will become too dominant at higher co-ordination, leading to population of only on-top sites. Strong π interactions favour higher co-ordination sites.

CO bound to Pt(111) submerged in 0.1 M HClO$_4$, exhibits an FTIR peak associated with a linearly bound on-top species at 2070 cm^{-1} [1]. 0.6 ML of Ru is deposited on the Pt(111) electrode to form islands of Ru. When CO is adsorbed on the resulting surface the peak at 2070 cm^{-1} shifts by -10 cm^{-1}, and decreases in intensity while a new peak appears at 1999 cm^{-1}. The new peak is shifted by $+6$ cm^{-1} compared to the peak associated with CO bound in an on-top site on a clean Ru electrode. Interpret the data as to where and how the CO is bound.

According to the Blyholder model of CO adsorption, the higher the frequency of the C–O stretch, the weaker the M–CO chemisorption bond. Accordingly, CO with a vibrational wavenumber of 1993 cm^{-1} is more strongly bound on clean Ru than on clean Pt, which has a wavenumber of 2070 cm^{-1}. The shift of -10 cm^{-1} as Ru is added to the Pt surface indicates an electronic effect in which coadsorbed Ru atoms strengthen the Pt–CO bond. The $+6$ cm^{-1} shift on Ru islands, compared to clean Ru, indicates that an electronic effect caused by the adsorption on Ru on Pt leads to a weakening of the Ru–CO chemisorption bond compared to chemisorption on the clean Ru surface. The electronic effect arises from charge transfer between Pt and Ru.

Since the CO is more strongly bound on Ru than on Pt, if CO were initially adsorbed on Pt and then Ru is added to the surface, the CO will migrate from Pt adsorption sites to Ru sites. Thus, the 2070 cm^{-1} peak will decrease in intensity after the deposition of Ru as CO migrates to Ru islands, while the accompanying 1999 cm^{-1} peak will grow in intensity.
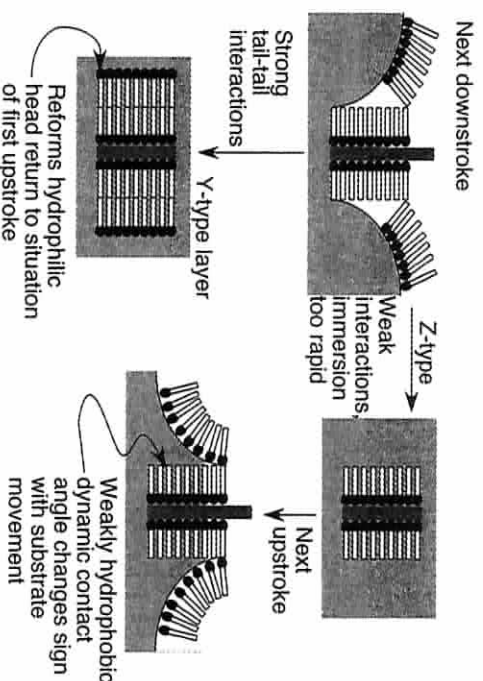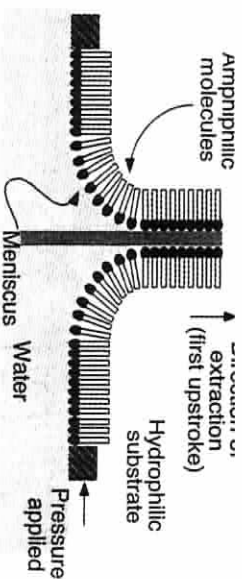
The time comes from

$$t = \frac{\theta \sigma_0}{s Z_w} = \frac{(0.01)(1 \times 1}{(9 \times 10^{-8})(1.56}$$

5.5 Your lab partner has prepared two Si crystals but h
other is terminated with an oxide layer. Propose a
from the surface and (2) solvent molecules must be
$CH_3(CH_2)_7SH$.

The sticking coefficient of $CH_3(CH_2)_7SH$ is ≈ 1 f
the sticking coefficient is significantly smaller bec

The oxide-terminated surface is an OH-terminate
surface is hydrophobic. They can be identified sir
surface that is wetted is OH-terminated whereas th
droplets.

5.6 Explain the observed trend that C_4 straight-chain
SAMs that exhibit a structure that is as well ordere

Whereas the interaction of the head group anch
in large part due to the non-covalent interactions b
in the C_4 amphiphiles are not sufficiently strong
excitations. The longer C_{12} chains have stronger
number of CH_2 groups that can interact with each
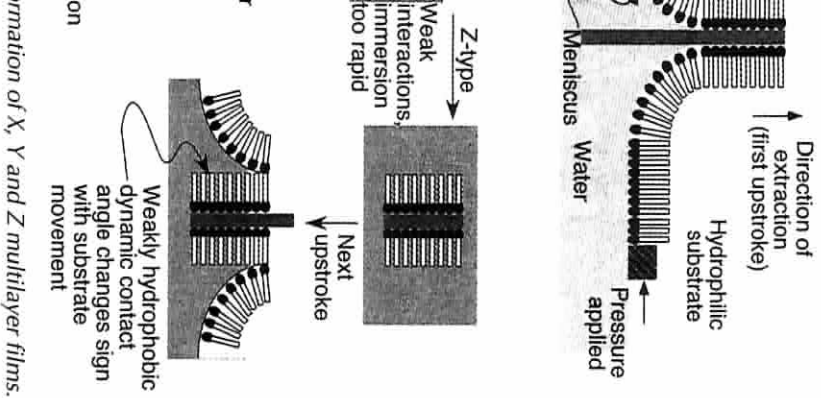overcome the destabilizing influence of other force

5.7 Describe what would occur during vertical depos
were stationary and a large surface area substrate v

The trough is a shallow rectangular tray filled v
carefully pipetting a dilute solution of the film-form
of the solvent the sweep is moved towards the floa
of the float is measured by a torsion balance. Thre

• *Gaseous films*: In films with very large surface
  like an ideal gas. The films can be regarded as a
  substrate.

• *Liquid film*: There exists a certain degree of c
  molecules. Two types have been observed: liqui
  type of film can be characterized by high comp
  show a first-order "liquid-gas" phase transitio
  expanded films.

• *Solid films*: The closest packing of the film-form
  further increased.

  As molecules deposit on the substrate, the num
  If the sweep is not moved towards the float to d
  areal density, the density will drop. As the densit
  the reverse order to those listed above, and becom

5.8 After a 4 h exposure to pure, deoxygenated H_2O,
an oxygen atom coverage of 0.6 ML measured

5.4 The sticking coefficient is defined as

$$s = r_{ads}/Z_w$$

and represents the probability of a successful adsorption event. The collision frequency in solution
is given by

$$Z_w = c_{sol}'(k_B T / 2 \pi m)^{1/2} \qquad (5.12.1)$$

where c_{sol} is the concentration in molecules per cubic metre. The initial sticking coefficient of
$CH_3(CH_2)_7SH$ on a gold film is 9×10^{-8}. Assuming a constant sticking coefficient, which is valid
only at low coverage, estimate the time required to achieve a coverage of 0.01 ML for adsorption
from a 5×10^{-3} mol l^{-1} solution. Take the surface density of atoms to be 1×10^{19} m^{-2}.
Concentration must be converted

$$c_{sol} = (5 \times 10^{-3} \text{ mol dm}^{-3}) \left(\frac{10^3 \text{dm}^3}{\text{m}^3} \right) (6.02 \times 10^{23} \text{ mol}^{-1}) = 3.01 \times 10^{24} \text{ m}^{-3}$$

The molecular weight is $M = 0.1463$ kg mol^{-1}. Then substitute R for k_B and Z_w is

$$Z_w = c_{sol} \left(\frac{RT}{2\pi M} \right)^{1/2} = 3.01 \times 10^{24} \left(\frac{8.3145 \times 298}{2\pi \times 0.1463} \right)^{1/2} = 1.56 \times 10^{26} \text{ m}^{-2} \text{ s}^{-1}$$

Figure Exercise 5.3 *The formation of X, Y and Z multilayer films.*

Amphiphilic molecules

Hydrophilic substrate

Meniscus Water

Pressure applied

extraction (first upstroke)

Next downstroke

Z-type

Weak interactions, immersion too rapid

Weakly hydrophobic dynamic contact angle changes sign with substrate movement

Next upstroke

Strong tail-tail interactions

Reforms hydrophilic head return to situation of first upstroke

Y-type layer

The time comes from $\theta\sigma_0 = sZ_w t$

The sticking coefficient of $CH_3(CH_2)_7SH$ is ≈ 1 for gas phase $CH_3(CH_2)_7SH$. From the solution, the sticking coefficient is significantly smaller because (1) solvent molecules must be displaced from the surface and (2) solvent molecules must be displaced from the solvation shell around the $CH_3(CH_2)_7SH$.

$$t = \frac{\theta\sigma_0}{sZ_w} = \frac{(0.01)(1 \times 10^{19})}{(9 \times 10^{-8})(1.56 \times 10^{26})} = 7.1 \times 10^{-3}\, s$$

5.5 Your lab partner has prepared two Si crystals but has not labelled them. One is H-terminated, the other is terminated with an oxide layer. Propose and explain an experiment you could perform in your kitchen that would distinguish the two.

The oxide-terminated surface is an OH-terminated surface and is hydrophilic. The H-terminated surface is hydrophobic. They can be identified simply by placing a drop of water on them. The surface that is wetted is OH-terminated whereas the H-terminated surface causes the water to form droplets.

5.6 Explain the observed trend that C_4 straight-chain amphiphile generally do not form LB films or SAMs that exhibit a structure that is as well ordered as that of C_{12} straight-chain amphiphiles.

Whereas the interaction of the head group anchors the molecule to the substrate, the ordering is in large part due to the non-covalent interactions between the chains. The chain–chain interactions in the C_4 amphiphiles are not sufficiently strong to overcome the disordering effects of thermal excitations. The longer C_{12} chains have stronger chain–chain interactions because of the greater number of CH_2 groups that can interact with each other. These interactions are strong enough to overcome the destabilizing influence of other forces.

5.7 Describe what would occur during vertical deposition of an LB film if the barriers of the trough were stationary and a large surface area substrate was used.

The trough is a shallow rectangular tray filled with the liquid substrate. The film is prepared by carefully pipetting a dilute solution of the film-forming material onto the substrate. After evaporation of the solvent the sweep is moved towards the float and the force necessary to maintain the position of the float is measured by a torsion balance. Three types of behavior can be described:

- *Gaseous films*: In films with very large surface area per molecule ($> 100\ Å^2$), the film behaves like an ideal gas. The films can be expanded or contracted without phase transitions. The gaseous film can be regarded as a dilute two-dimensional solution of the film-forming material and the substrate.

- *Liquid film*: There exists a certain degree of cooperative interaction between the film-forming molecules. Two types have been observed: liquid expanded and liquid condensed films. The first type of film can be characterized by high compressibility and the absence of islands. These films show a first-order "liquid-gas" phase transition. Condensed films are formed by compressing expanded films.

- *Solid films*: The closest packing of the film-forming material is realized if the surface pressure is further increased.

As molecules deposit on the substrate, the number of molecules in the Langmuir film decreases. If the sweep is not moved towards the float to decrease the surface area and maintain a constant areal density, the density will drop. As the density drops the film will undergo phase transitions in the reverse order to those listed above, and become progressively less well ordered.

5.8 After a 4 h exposure to pure, deoxygenated H_2O, a H-terminated Si(111) surface is found to have an oxygen atom coverage of 0.6 ML, measured with respect to the number of Si atoms in the

--- left margin column ---

Direction of
extraction
(first upstroke)

Z-type →

Hydrophilic
substrate

Meniscus

Water

Pressure
applied

Weak
interactions,
immersion
too rapid

Weakly hydrophobic
dynamic contact
angle changes sign
with substrate
movement

↓Next
upstroke

$s = r_{ads}/Z_w$

ssful adsorption event. The collision frequency in solution

$$(5.12.1)$$

$= c_{sol}(k_BT/2\pi m)^{1/2}$

$$(5.12.2)$$

cules per cubic metre. The initial sticking coefficient of
8. Assuming a constant sticking coefficient, which is valid
required to achieve a coverage of 0.01 ML for adsorption
the surface density of atoms to be $1 \times 10^{19}\ m^{-2}$.

rmation of X, Y and Z multilayer films.

$10^{24}\left(\frac{8.3145 \times 298}{2\pi \times 0.1463}\right)^{1/2}$ kg mol^{-1}. Then substitute R for k_B and Z_w is

$10^3\, \frac{dm^3}{m^3}$ $(6.02 \times 10^{23}\ mol^{-1}) = 3.01 \times 10^{24}\ m^{-3}$

$= 1.56 \times 10^{26}\ m^{-2}\ s^{-1}$

(b) Isolated heteroatoms on the terraces have no effect upon the release rate from the steps. However, they may act as nucleation centres. If the heteroatoms are effective at providing nucleation sites, island growth will be preferred to step flow growth. If the heteroatoms are ineffectual at providing nucleation sites, they will not change the growth mode.

7.3 Si is the most important semiconductor for electronic applications. GaAs and its III–V sister compounds are better suited than Si as building blocks for optical devices such as light emitting diodes (LEDs) and lasers. The integration of optical components with electronics is a highly desirable manufacturing goal for improved communications, computing and display devices. Discuss fundamental physical reasons why it is difficult to integrate GaAs circuitry with Si.

GaAs assumes a different crystal structure than Si because it has two different types of atoms. Forcing GaAs to assume a diamond lattice with the same spacing as Si would result in a great deal of strain because of the different atomic sizes of Ga and As as compared to Si. One would expect a growth mode (Volmer–Weber) in which 3D islands form from the start. Therefore, circuitry that requires epitaxial growth of smooth layers will be difficult to achieve.

7.4 Discuss how Auger electron spectroscopy or XPS can be used to distinguish Frank–van der Merwe from Volmer–Weber growth. Hint: Look at Fig. 2 and consider how the substrate signal varies.

In the FM growth mode , the substrate is covered in a layer-by-layer fashion. In VM growth, 3D islands form. For both AES and XPS, the substrate signal is attenuated with increasing growth due to inelastic scattering of the photoelectrons in the adsorbed layer. In FM growth, the signal is the sum of substrate atoms covered by n adsorbate layers plus the signal of substrate atoms covered by $n-1$ atoms. The resulting attenuation is linear in adsorbate coverage for each layer and will show a break in the slope of a plot of the intensity of the substrate signal versus the intensity of the adsorbate signal when the adsorbate coverage reaches 1 ML. Progressively weaker break points are observed as each successive layer is completed.

In WM growth, the substrate signal is composed of a series of terms from bare surface + covered by one layer + covered by two layers +…. The slope of a plot of substrate versus adsorbate signal decreases monotonically (without break points) and does not decrease as rapidly as for FM growth.

7.5
(a) Consider the epitaxial growth by MBE of $In_{0.67}Al_{0.33}P$ layer on an InGaAs substrate. What must the relative fluxes of In, Al and P be in order to maintain this composition? What influence does the substrate temperature have on epitaxy and the required fluxes?

(b) Consider the CVD growth of P-doped (at a concentration of 10^{16} cm^{-3}) $Si_{(1-x)}Ge_x$ with $x = 0.05$ from the respective hydrides. Discuss the influence of surface temperature on epitaxy and the fluxes required to maintain this composition.

(a) In MBE, the pure elements In, Al and P are evaporated from solid sources. The temperature of the evaporators is adjusted to achieve the required flux. In this case, a relative flux of In: Al: P of 0.67: 0.33: 0.75 will yield approximately the correct film composition because the sticking coefficients of the three components are all ≈ 1. Slight corrections to the relative fluxes might have to be made to correct for deviations from unit sticking coefficients.

The temperature of the substrate is adjusted to allow for adequate diffusion. If T_s is too low, the diffusion rate will not be sufficiently high for epitaxy to occur. Higher deposition rates demand greater diffusion and, thus, higher T_s. However, T_s does not have an effect on the required relative fluxes. An exception is if T_s is raised so high that one component, e.g. In, begins to desorb. The temperature must also not be raised so high that interdiffusion (diffusion of adlayers into the substrate) begins to occur.

(b) In CVD of these layers, SiH_4, GeH_4 and PH_3 must adsorb and decompose at the surface. Si, Ge and P then must diffuse sufficiently to grow epitaxially. H atoms must desorb as H_2 from the surface, otherwise they will block sites and effectively poison the decomposition reactions.

Answers to E[...]

The adsorption of SiH_4 and GeH_4 is activated a complicated function of T_s and the fluxes, si must all be considered.

It is impossible for any arbitrary T_s to say w the desired composition without a calculation such that the rate of desorption of H_2 is equal the hydrides and the sticking coefficients have close to unity), then the flux of SiH_4 to GeH$_4$ s for differences in the sticking coefficients) and the SiH_4 flux. (10^{23} cm^{-3} is the typical order

7.6 The dimensionless formation energy $E(V)$ of a dimensionless volume is given by

$$E(V) = -\alpha V + \frac{2\beta V^{2/}}{e^{1/2}}$$

The chemical potential of an island is given by

$$\mu(V) =$$

Assuming that $\alpha = 0$, predict the most probable i The most probable island volume is given when derivative yields

$$\mu(V) = \frac{dE(V)}{dV} = -\alpha + \frac{4\beta}{3e^{1/3}} V^{-1/}$$

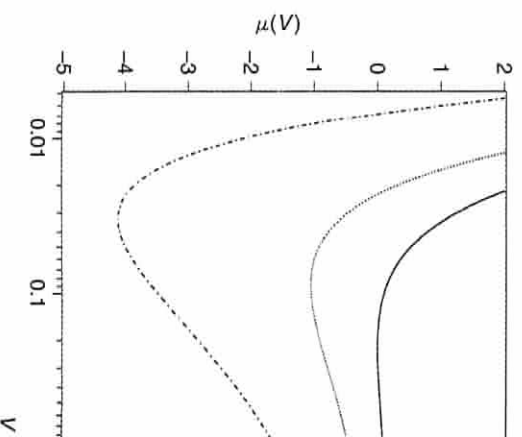The fourth term is missing from the original re below and is identical to Fig. 7.18. It shows that increases.

Figure Exercise 7.6 Plots of chemical potential versus th

The adsorption of SiH_4 and GeH_4 is activated and, therefore, T_s dependent. The growth rate is a complicated function of T_s and the fluxes, since adsorption as well as desorption and diffusion must all be considered.

It is impossible for any arbitrary T_s to say what exactly the relative fluxes must be to achieve the desired composition without a calculation of the kinetics. In the limit of high temperature such that the rate of desorption of H_2 is equal to or greater than the rate of adsorption of any of the hydrides and the sticking coefficients have reached their saturation values (which should be close to unity), then the flux of SiH_4 to GeH_4 should be roughly 0.95: 0.05 (subject to correction for differences in the sticking coefficients) and the flux of PH_3 will be $\approx 10^{16}/10^{23} \approx 10^{-7}$ of the SiH_4 flux. (10^{23} cm^{-3} is the typical order of magnitude for the density of a solid.)

7.6 The dimensionless formation energy $E(V)$ of a single-faceted quantum dot as a function of its dimensionless volume is given by

$$E(V) = -\alpha V + \frac{2\beta V^{2/3}}{e^{1/2}} - 2V^{1/3}\ln(e^{1/2}V^{1/3}) \qquad (7.16.1)$$

The chemical potential of an island is given by

$$\mu(V) = \frac{dE(V)}{dV}$$

Assuming that $\alpha = 0$, predict the most probable island volume for $\beta = 1.36, 0.7$ and -0.7.

The most probable island volume is given when the chemical potential is minimized. Taking the derivative yields

$$\mu(V) = \frac{dE(V)}{dV} = -\alpha + \frac{4\beta}{3e^{1/3}}V^{-1/3} - \frac{2}{3}V^{-2/3}\ln(e^{1/2}V^{1/3}) - \frac{2}{3}V^{-2/3} \qquad (7.16.2)$$

The fourth term is missing from the original reference. This function is plotted in Fig. Ex. 7.6 below and is identical to Fig. 7.18. It shows that the minimum moves to greater values of V as β increases.
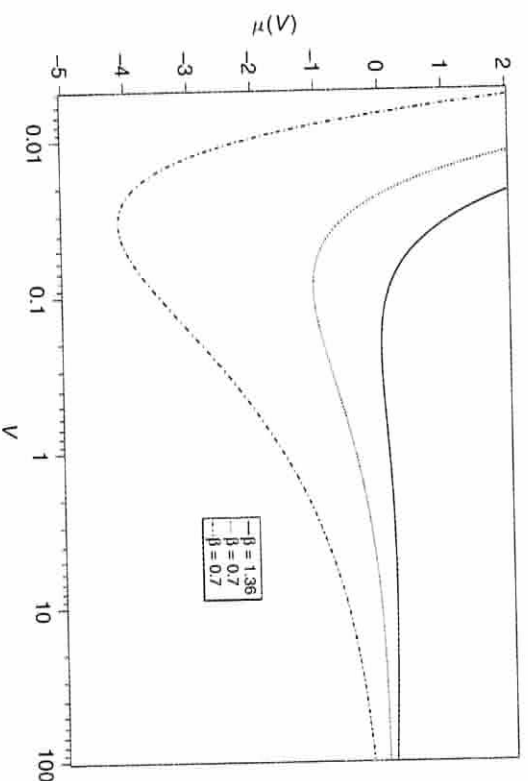

Figure Exercise 7.6   Plots of chemical potential versus the size of a quantum dot for different values of β.