

A T O M S A N D M O L E C U L E S

A T A S O L I D S U R F A C E

by
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for the degree
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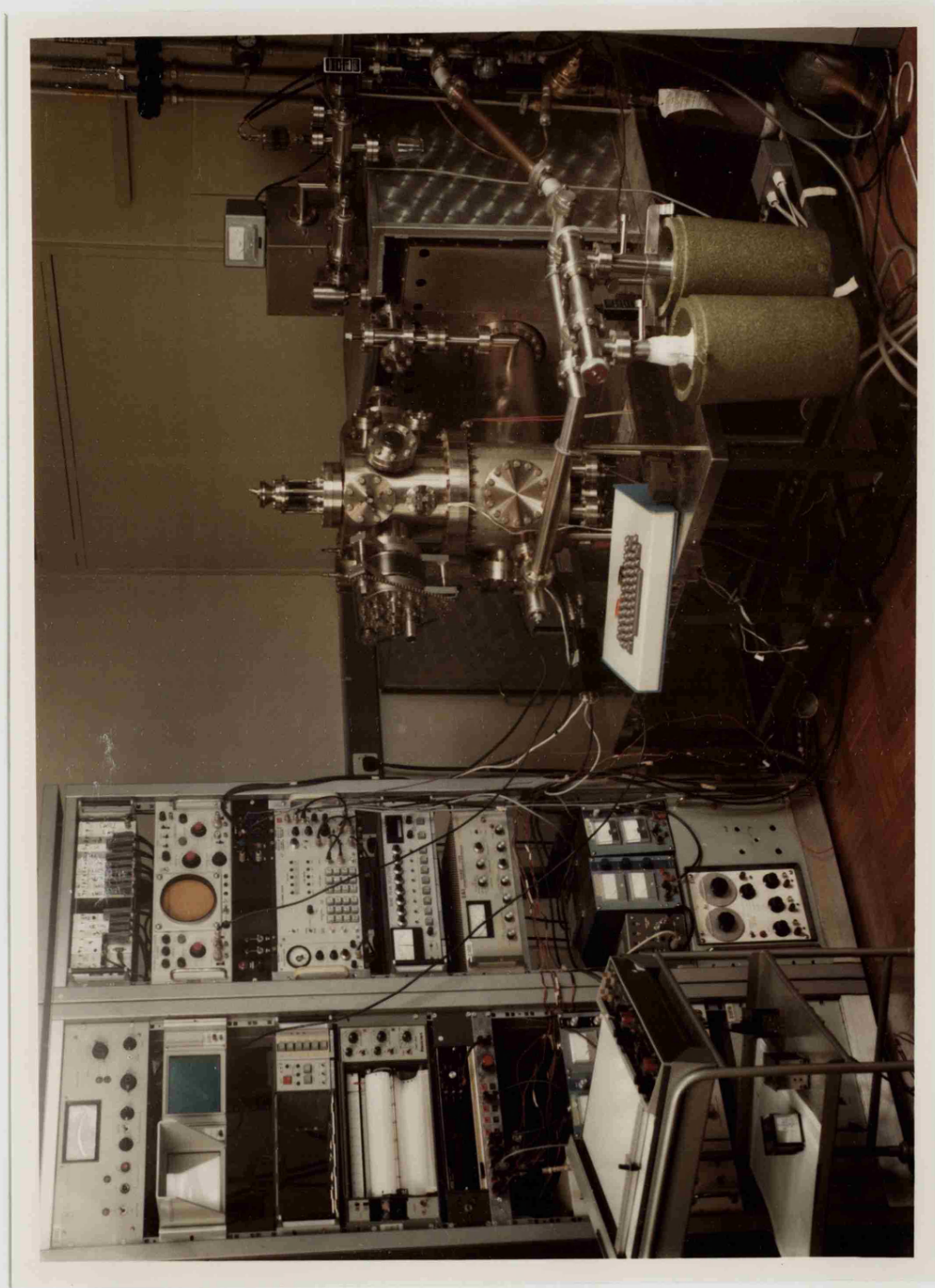


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THE ULTRA-HIGH-VACUUM EXPERIMENTAL SYSTEM USED FOR
THE TIME-OF-FLIGHT STUDY PRESENTED IN CHAPTER V

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"It is a capital mistake to theorize

·before one has data."

Sherlock Holmes

Scandal in Bohemia.

ABSTRACT

Some aspects of the interaction of gas-atoms and solid-surfaces are presented. By using simple mathematical models, an intuitive understanding of the interaction between atoms and surfaces has been achieved. By a logical extension of such techniques, it is shown how a general theory for the desorption of atoms from surfaces may be formulated. Potential parameters for the gas-surface interaction are deduced for a number of experimental systems using the published data for the surface residence times of adsorbed atoms.

The growth of thin semiconducting films by Molecular Beam Epitaxy is described and the results of kinetic studies for the interaction of Ga and As₄ beams with a GaAs (100) surface are discussed. By adopting some of the previously developed atomistic concepts, a microscopic model is proposed which explains some of the fundamental aspects of the growth mechanism employed by this method.

As part of the kinetic study of Molecular Beam Epitaxy, the time-of-flight technique for measuring the velocity distribution of a beam was used. This method has been studied experimentally and detailed results are presented for As₄ and Pb neutral beams. It is shown that when a quadrupole mass spectrometer with a cross beam ionizer is employed as a detector, serious errors arise from inherent time delays, which are observed to be strong functions of several operating parameters. The consequence of this instrument malfunction is discussed with particular reference to the measurement of energy accommodation coefficients.

Chapter I

INTRODUCTION

a) Why Surfaces?

When compared to the many other branches of the physical sciences, surface physics is a comparative infant. For example, the study of bulk physical properties has been in progress for many centuries, however it is rather ironic that in order to sample any bulk property experimentally, one must also sample the effects of at least one surface. Theoretically surface effects have long been regarded as being "second order", and it is only within the last fifty years that some of the many varied properties associated with surfaces have begun to be understood.

The foundations of surface physics were laid down by experimentalists in the early part of this century, but unfortunately progress was slow. It was not possible for early workers to prepare their samples in any consistent manner, and it was not until the 1950's, with the introduction of ultra high vacuum (UHV) technology, that major advances could be made. The reason for this may be illustrated by referring to the kinetic theory of gases. The flux of molecules striking a surface is given by:

$$F(\text{molecules/cm}^2/\text{sec}) = 3.52 \times 10^{22} \frac{P(\text{torr})}{\sqrt{MT(K)}}$$

where M is the molecular weight of the ambient gas at temperature T . At atmospheric pressure and room temperature for example, F is typically in the range of 10^{23} molecules/cm²/sec. On average, a surface has approximately 10^{15} atoms/cm² and consequently

if every atom incident upon the surface were to "stick", then clearly experiments on uncontaminated surfaces would be quite impossible. To overcome this problem it is customary for surface experiments to be performed under UHV conditions, where the base pressure is typically 10^{-10} Torr. In such a system a surface will remain "clean" for 10^4 seconds.

The study of surface physics has many applications in current technology. It is, for example, only recently that some of the problems associated with catalysis have been linked to possible surface effects. Methane is produced commercially via the reaction of H_2 and CO with a nickel catalyst. Why specifically nickel is so suitable is thought to be due to the complex processes that occur between the reaction species, and that surface. Within the solid state electronics industry the quest has long been for high quality, topographically perfect semiconductor crystals. The performance of thin film devices such as impact avalanche transit time (IMPATT) diodes, and field effect transistors (FET's) is critically dependent upon such features as the uniformity of doping, and the crystalline perfection within $5000 \text{ \AA}$ of the surface. With such stringent requirements, the development of well controlled growth processes is vital and only when a detailed knowledge of the interaction between atoms and surfaces is available, will this become possible.

b) Surface Structure

When a perfect crystal is cleaved, it is possible to create two surfaces, each containing ordered arrays of atoms often having the same symmetry and atomic positions as the original lattice. Such surfaces however are not always stable and, to minimise their surface free energy, undergo a surface reconstruction process whereby the atomic positions are slightly modified with

respect to their initial configuration. The (111) face of silicon is a good example of such surface reconstruction. When cleaved in vacuum, the surface exhibits a $(2 \times 1)^{\dagger}$ symmetry, yet after heating to 640 K the surface undergoes a spontaneous phase transition to a (7×7) structure (1). Clean alkali-halide crystals are rather opposite in character; when cleaved in vacuum the observed single crystal faces are those expected from an abrupt termination of the bulk crystal (2).

Such structural identification is now quite routine in surface physics, although theoretically no quantitative understanding of reconstruction yet exists. The proposal that surface vacancies or foreign atoms might stabilize such surfaces, has encouraged experimentalists to perform detailed studies of adsorption systems. Suppose that in a particular experiment some atoms are adsorbed onto a clean surface; the location of these atoms will depend critically upon the surface condition at the time of adsorption. It has subsequently been proposed (4) that the Si (111)- (7×7) structure is stabilized by the presence of aluminium impurities, and, that an additional structure Si (111)- (5×5) is associated with the presence of gold (5).

c) Electrons at Surfaces

Clearly in order to understand the many complicated processes occurring at an interface, a detailed knowledge of the local electron distribution is required. Much experimental work is at present being undertaken in this area of surface science and a few of the techniques currently employed are presented in table (I.1).

No attempt will be made to describe each of these techniques in detail, but generally speaking it is normal for the

[†] Throughout this thesis the two-dimensional crystallographic notation is that of E. Wood (3).

Incident Particle	Emergent Particle		
	XR	e ⁻	IONS
UV	-	UPS	PD
XR	XRF	XPS	-
e ⁻	APS	AES, LEED	ED
IONS	IEX	INS	ISS, SIMS

UPS - Ultraviolet Photoelectron Spectroscopy
 PD - Photodesorption
 XRF - X-ray Fluorescence
 XPS - X-ray Photoelectron Spectroscopy
 APS - Appearance Potential Spectroscopy
 AES - Auger Electron Spectroscopy
 LEED - Low Energy Electron Diffraction
 ED - Electron Desorption
 IEX - Ion Excited X-rays
 INS - Ion Neutralisation Spectroscopy
 ISS - Ion Scattering Spectroscopy
 SIMS - Secondary Ion Mass Spectroscopy

Table I.1 Methods of Surface Analysis

incident beam of particles to be monoenergetic with a well defined trajectory with respect to the surface; the emergent beam is then both energy and spatially analysed (6). Each technique provides its own characteristic information about a particular aspect of the surface. For example, the distribution of occupied electronic states in the valence band may be obtained with UPS, whereas AES provides a chemical analysis of the surface. To obtain detailed information about a particular surface it is common to perform several types of analysis within the same experimental system.

Theoretically the detailed explanation of data from such experiments is still beyond present capabilities. It was believed for example, that LEED data could be directly inverted in the same way as bulk crystallographic x-ray data, to give precise knowledge of the positions of atoms in the surface unit cell. The first theory to attempt this was published by Bethe in 1928 (7); now 48 years later, it is still not possible to unambiguously evaluate atomic positions with any confidence. It is perhaps rather ironic that the reason why LEED is so useful as a surface sensitive technique, is also the reason why no adequate theory exists to interpret the experimental data. The large inelastic electron scattering cross section of the atoms in the solid has the consequence that any electrons which are elastically back-scattered from the sample, must emanate from within a few lattice spacings of the surface. Unfortunately however, no satisfactory inelastic electron scattering theory exists and consequently any theoretical analysis of LEED intensities is at best rather poor.

d) Atoms at Surfaces.

Even if a detailed knowledge of the local electron distribution were available, the complete description of the

interaction between an atom and a surface would still be remote. Progress has been made in this difficult field by calculating the scattering from model gas atom-surface potentials and comparing the results with experimental data.

When a gas atom collides with a surface, a wide variety of processes is possible. The distribution of scattered atoms is a function of the energy and trajectory of the incident atom, the constitution and temperature of the surface, and the strength of the gas-surface interaction. In a typical scattering experiment it is possible to define the initial parameters of both the incident beam and those of the surface: by measuring the resulting distribution of scattered atoms it is possible to discover valuable information relating to the gas-surface interaction (9).

Figure (I.1) shows a schematic diagram of such an interaction potential based upon a calculation using the Born-Oppenheimer approximation and the pairwise addition of model gas atom-surface potentials. Far from the surface the incident atom feels a mildly attractive force which arises from a Van der Waals interaction between this atom and each of the atoms in the surface. Close to the surface the incident atom is repelled by localised short range forces as the electron clouds of the incident atom and the surface atoms begin to overlap. Necessarily, therefore, at a certain distance from the surface, the potential has a minimum value where the gas atom is in equilibrium with the surface.

Figure (I.2) shows some of the possible trajectories for an atom interacting with a surface. (1) shows the gas atom being elastically scattered from the surface. In such an event, momentum may be transferred to the atom in discrete amounts from the lattice, the resulting distribution of atoms being analogous to the familiar diffracted beams obtained when x-rays scatter from

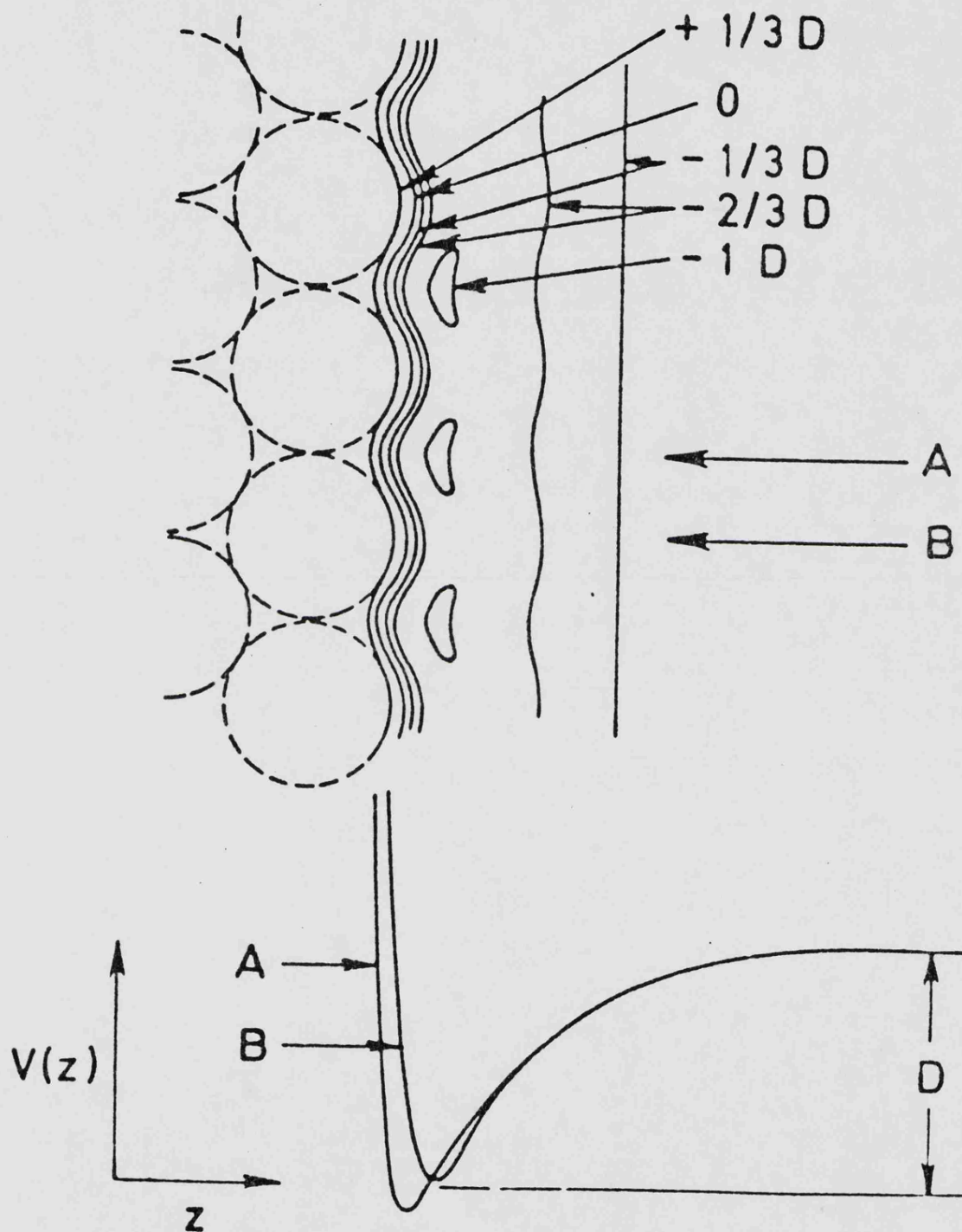


Figure I.1 The gas atom-surface potential

a crystal. In each of the other possible cases (2-4) the scattering is inelastic. (2) shows the resulting trajectory when an atom transfers a small fraction of its incident energy to the surface by phonon creation. (3) shows the rather more extreme consequences when so much of the initial energy has been transferred, that the atom is trapped within the long range attractive potential. The atom is unable to completely escape, but it retains enough energy to migrate across the surface. In (4) the incident atom has lost still more of its energy, so that it is trapped or adsorbed. It is possible that while in states (3) or (4), the resident atom may receive enough energy from the random thermal fluctuations at the surface, for it to escape. When liberated in this fashion the atom is said to be thermally desorbed.

In principle, each of these processes can be studied experimentally to provide detailed information about a particular surface property. Diffractive atom scattering, for example, may provide data on atomic positions (9), and in fact compliment the results obtained by one of the various electron spectroscopies. If a thermal beam of atoms is adsorbed on to a surface, it is possible to measure the average length of time, τ , that an atom resides before desorbing. By measuring τ , as a function of the surface temperature, T , it is possible to evaluate the well depth, D , of the atom-surface potential (10) (figure I.1), because it is known experimentally that,

$$\tau = \tau_0 \exp \frac{D}{k_B T} \quad (1.1)$$

Here τ_0 is a pre-exponential factor which has a value of approximately the mean surface-atom vibration time ($\sim 10^{-13}$ sec) and k_B is Boltzmann's constant. The mean energy of the thermally desorbing beam is specified by the accommodation coefficient, α .

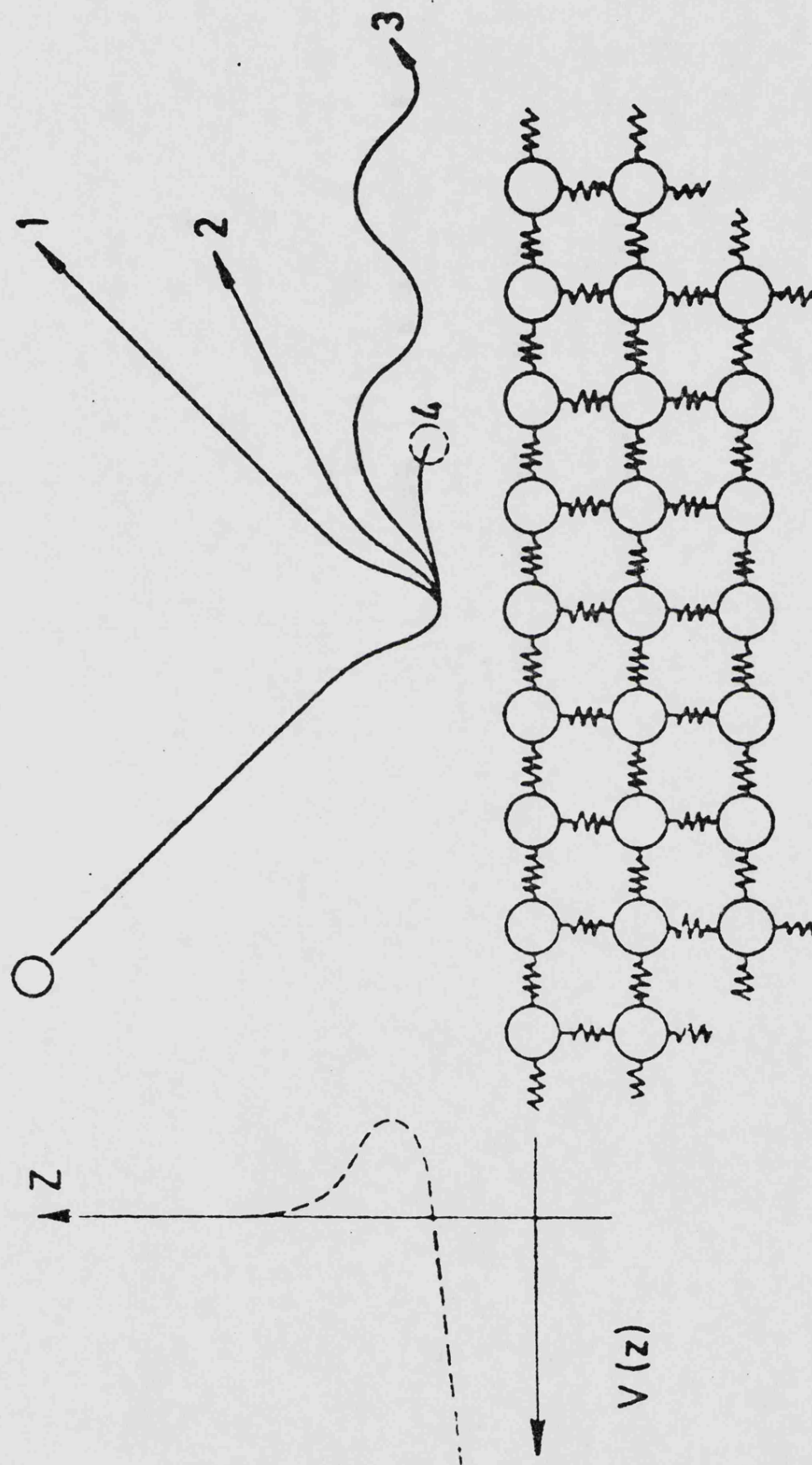


Figure I.2 Trajectories for some common atom-surface collision processes

If the average energy of an impinging atom is E_i and that of the desorbing atom is E_o , then the accommodation coefficient is defined:

$$\alpha = \frac{E_o - E_i}{E_s - E_i} \quad (1.2)$$

where E_s is the average energy of a beam which is in thermal equilibrium with the surface. If the beam comes off with the temperature of the surface, then $\alpha = 1$ and the beam is then said to be fully accommodated.

Theoretically the scattering of atoms from solid surfaces has received much attention. Broadly speaking such work falls into two categories which are defined by the gas atom-surface interaction time. If this time is less than $\sim 10^{-12}$ seconds then the incident atom is effectively reflected by the surface (12). The scattered beam is then predominantly governed by the parameters of the incident beam; this is the realm of atom diffraction. For longer times the atom is adsorbed on to the surface and undergoes many surface oscillations before eventually desorbing. Accommodation is complete, and the spatial distribution of the desorbed flux normally follows the familiar "cosine" law (13). Each regime has received detailed investigation in both the classical and quantum mechanical limits and numerous reviews exist which discuss the requirements of a satisfactory theory (14, 15).

e) Outline of this Thesis.

In this thesis an attempt will be made to explain some of the features associated with the interaction of atoms and molecules with solid surfaces. Much of the work has already been published and appears as appendices. This work is presented in a unified manner in the following chapters and unnecessary duplication has been intentionally avoided.

In chapter II a one-dimensional model of a surface is introduced. The modes of vibration and atomic displacements are explicitly calculated for this model and the emergence of modes that originate solely from the presence of a surface are discussed. The rate of desorption is calculated for an atom interacting with this surface via a cut-off harmonic potential.

In chapter III this model is generalized to three dimensions and again the rate of desorption is formulated. Features arising from the additional degrees of freedom are discussed and a comparison with the one-dimensional model is made. The limitations of the calculation are presented with particular emphasis on the inadequacy of the cut-off harmonic potential. A derivation of the surface delay time is then given for an atom interacting with a perfectly general three dimensional substrate via a general potential. Comparison with experimental data for a variety of adsorption systems is made with a discussion of how various surface features might affect the choice of interaction potential.

In chapter IV the growth of thin film semiconductor compounds by molecular beam epitaxy is introduced. Using this technique it is possible to grow epitaxially perfect layers and, by gaining a greater insight into the growth mechanism, it is hoped that better control of dopant incorporation may be established. Studies of the kinetic parameters which determine growth have been made with particular emphasis on the fabrication of the III-V semiconductor gallium arsenide. Using published kinetic data, a model describing the interaction of Ga and As₄ beams with a GaAs (100) surface is presented. By contrasting this model with the atomistic calculation of chapter III it is possible to highlight some of the complexities associated with the interaction of molecules with surfaces.

In chapter V an experimental study of the energy exchange processes between a molecular beam and a surface is presented. In such an experiment it is essential to be able to measure the velocity distribution of the scattered beam to a reasonable degree of accuracy, and it is common to use a time of flight technique for this purpose. The basic philosophy of this method and its application to atom-surface scattering is discussed. The experimental results obtained indicate that when a quadrupole mass spectrometer is used as a detector in such an experiment, the measured velocity distribution is critically dependent upon the operating parameters of the instrument.

Chapter II

ONE DIMENSIONAL HARMONIC CHAIN

a) Background

The model chosen here to represent the interaction of an atom with a solid surface, is the one-dimensional harmonically coupled chain. This model is not new to physics and it was Newton (16) who first chose this system to represent a lattice. The dynamics of linear chains have subsequently been studied extensively in the theory of solids, and have been useful as a precursor to more realistic calculations (17). This is the aim of the work presented in this chapter.

To date most calculations have been performed for systems with effectively an infinite number of point masses. In practice this is achieved by using cyclic boundary conditions (18) which restrict the vibrational amplitude of the N^{th} particle to be precisely the same as that of the first. The dispersion relation for such a system will in general be grouped into distinct bands, the number of bands being equal to the basis of the unit cell. These band modes represent waves which propagate through the lattice, the particle displacements being sinusoidal. For a diatomic system for example, the frequencies are grouped into two bands commonly referred to as the optical and acoustic branches (19).

For the finite harmonic chain it is not possible to use periodic boundary conditions, as although considerably simplifying the calculation, their use would prevent the study of surface phenomena. Born studied the finite monatomic chain and by solving the equations of motion obtained the dispersion relation and

expressions for the particle displacements (20). Each frequency represented a wave propagating along the lattice. Wallis investigated the effects of free ends on the vibrational frequencies of a one-dimensional diatomic lattice (21). He showed that besides the band modes expected from the infinite system, a series of extra modes appeared, their existence being dependent upon the mass ratio and the number of particles in the chain. Such "surface" modes are located in the gap between the optical and acoustic bands, and may be interpreted as waves which decay exponentially into the lattice (22).

Surface modes of vibration are analogous to electronic surface states (23), both being an effect of the collapse of periodicity at an interface. The experimental verification of the existence of such modes (24) has subsequently given rise to much speculation as to their contribution to various physical properties. It has, for example, been proposed that surface modes might play a dominant role in the scattering of a gas atom by a solid surface (25).

b) The vibrations of a finite chain.

Consider a diatomic chain of $2N$ particles composed of alternate masses M and m which interact via near neighbour harmonic forces of constant κ . The equations of motion are:

$$\begin{array}{rcl}
 M \ddot{x}_1 & = & \kappa (x_2 - x_1) \\
 \vdots & & \vdots \\
 m \ddot{x}_{2i} & = & \kappa (x_{2i+1} - x_{2i}) - \kappa (x_{2i} - x_{2i-1}) \\
 M \ddot{x}_{2i+1} & = & \kappa (x_{2i+2} - x_{2i+1}) - \kappa (x_{2i+1} - x_{2i}) \\
 \vdots & & \vdots \\
 \vdots & & \vdots \\
 m \ddot{x}_{2N} & = & -\kappa (x_{2N} - x_{2N-1})
 \end{array} \quad 1 \leq i \leq N-1 \quad (2.1)$$

where x_i denotes the displacement of the i^{th} atom from its equilibrium position. In the α^{th} mode, each atom oscillates sinusoidally with frequency ω_α , so that;

$$\ddot{x}_i = -\omega_\alpha^2 x_i \quad (2.2)$$

On substitution of (2.2) into (2.1) a set of linear homogeneous equations is obtained, the solutions of which must satisfy;

$$\begin{vmatrix} \omega^2 - \kappa \left[\frac{1}{m} + \frac{1}{M} \right] & \frac{\kappa}{m} & 0 & \dots & 0 \\ \frac{\kappa}{M} & \omega^2 - \kappa \left[\frac{1}{m} + \frac{1}{M} \right] & \frac{\kappa}{M} & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \frac{\kappa}{M} & \dots & \dots & \omega^2 - \kappa \left[\frac{1}{m} + \frac{1}{M} \right] \end{vmatrix}_{2N-1} = 0 \quad (2.3)$$

where the $\omega = 0$ mode has been removed from the secular determinant and the eigenvectors are column vectors of relative displacements. The solutions representing propagating waves have frequencies

$$\omega_\alpha^2 = \kappa \left[\frac{1}{m} + \frac{1}{M} \right] \pm \sqrt{\kappa^2 \left[\frac{1}{m^2} + \frac{1}{M^2} \right] + \frac{2\kappa^2}{mM} \cos \frac{\pi \alpha}{N}} \quad 1 \leq \alpha \leq N-1 \quad (2.4)$$

the positive sign corresponding to the optical band, the negative sign the acoustic band. The relative displacements of the particles when in the α^{th} mode are;

$$x_{2g}^a - x_{2g-1}^a = - \left[\frac{1}{N} \right]^{\frac{1}{2}} \sin \left\{ (2g-1) \frac{\alpha\pi}{2N} \right\} \cos(\omega_a t - \phi_a)$$

$$1 \leq g \leq N$$

$$x_{2g+1}^a - x_{2g}^a = - \left[\frac{1}{N} \right]^{\frac{1}{2}} \sin \left\{ g \frac{\alpha\pi}{N} \right\} \cos(\omega_a t - \phi_a) \quad 1 \leq g \leq N-1$$

(2.5)

where the amplitudes are normalised so that

$$\sum_{i=2}^N (x_i^a - x_{i-1}^a)^2 = \cos^2(\omega_a t - \phi_a)$$

(2.6)

Here ϕ_a is a phase factor, as yet undetermined. From equation (2.4) clearly there are $(2N-2)$ band-like modes of vibration for the finite system. For a $2N$ particle system there are $2N$ independent modes of vibration and the final modal solution ($\omega = 0$ is the trivial solution) is:

$$\omega_s^2 = \kappa \left[\frac{1}{m} + \frac{1}{M} \right]$$

(2.7)

the relative displacements being

$$x_{2g} - x_{2g-1} = \frac{(-1)^g}{\sum_{n=1}^N \sqrt{\left(\frac{M}{m}\right)^{2n-2}}} \left[\frac{M}{m} \right]^{g-1} \cos(\omega_s t - \phi_s)$$

$$1 \leq g \leq N$$

$$x_{2g+1} - x_{2g} = 0 \quad 1 \leq g \leq N-1$$

(2.8)

the normalisation again satisfying equation (2.6). A plot is shown in figure (II.1) of the relative displacement of pairs of particles when the lattice vibrates in this surface mode. The

lighter of the two atoms is the atom labelled 1 and the relative displacement of this and the heavier atom 2 far exceeds any subsequent displacement. On the same scale a typical bulk amplitude might be ~ 0.1 .

For general adsorption systems it is perhaps more instructive to evaluate the vibrational modes of an impurity mass adjoining a diatomic chain. If the impurity has mass Q and also acts via a near neighbour harmonic interaction of strength κ , then the equations of motion are:

$$\begin{array}{rcl}
 Q \ddot{x}_1 & = & \kappa (x_2 - x_1) \\
 \vdots & & \vdots \\
 M \ddot{x}_{2i} & = & \kappa (x_{2i+1} - x_{2i}) - \kappa (x_{2i} - x_{2i-1}) \\
 m \ddot{x}_{2i+1} & = & \kappa (x_{2i+2} - x_{2i+1}) - \kappa (x_{2i+1} - x_{2i}) \\
 \vdots & & \vdots \\
 M \ddot{x}_{2N} & = & -\kappa (x_{2N} - x_{2N-1})
 \end{array} \quad 1 \leq i \leq N-1$$

(2.9)

By defining modal solutions as before and substituting from equation (2.2) the secular determinant is

$$\begin{vmatrix}
 \frac{Q}{\kappa} \omega^2 - 1 & 1 & & & 0 \\
 1 & \frac{M}{\kappa} \omega^2 - 2 & 1 & & \\
 & 1 & \ddots & \ddots & \\
 & & \ddots & \frac{m}{\kappa} \omega^2 - 2 & \ddots \\
 0 & & & \ddots & 1 & \frac{M}{\kappa} \omega^2 - 1
 \end{vmatrix}_{2N} = 0$$

(2.10)

which may be expanded to give (26)

$$\frac{v}{z^2 - z^{-2}} \left\{ \sqrt{\frac{u}{v}} [z^{2u+1} - z^{-(2u+1)}] + \left(\frac{u}{v} + b \right) [z^{2u} - z^{-2u}] \right. \\ \left. + b \sqrt{\frac{u}{v}} [z^{2u-1} - z^{-(2u-1)}] \right\} = 0 \quad (2.11)$$

where

$$u = \frac{m\omega^2}{\kappa} - 2 \\ v = \frac{M\omega^2}{\kappa} - 2 \\ b = \frac{\omega^2}{\kappa} (Q - m) + 1 \\ x = \frac{\sqrt{uv}}{2} \\ z = x + \sqrt{x^2 - 1} \quad (2.12)$$

This equation may be solved numerically (e.g. by the half interval search method), to find the modal frequencies, which in turn may be used to numerically evaluate the relative displacements. Figure (II.2) shows the solutions for the frequencies of such a system, as a function of the impurity mass. II.2(a) shows that when the impurity replaces a heavy atom it is possible to excite three independent surface modes, two within the forbidden gap and a third above the optical band. II.2(b) shows that when the impurity replaces the lighter atom only one surface mode can be excited, its frequency being a function of the impurity mass.

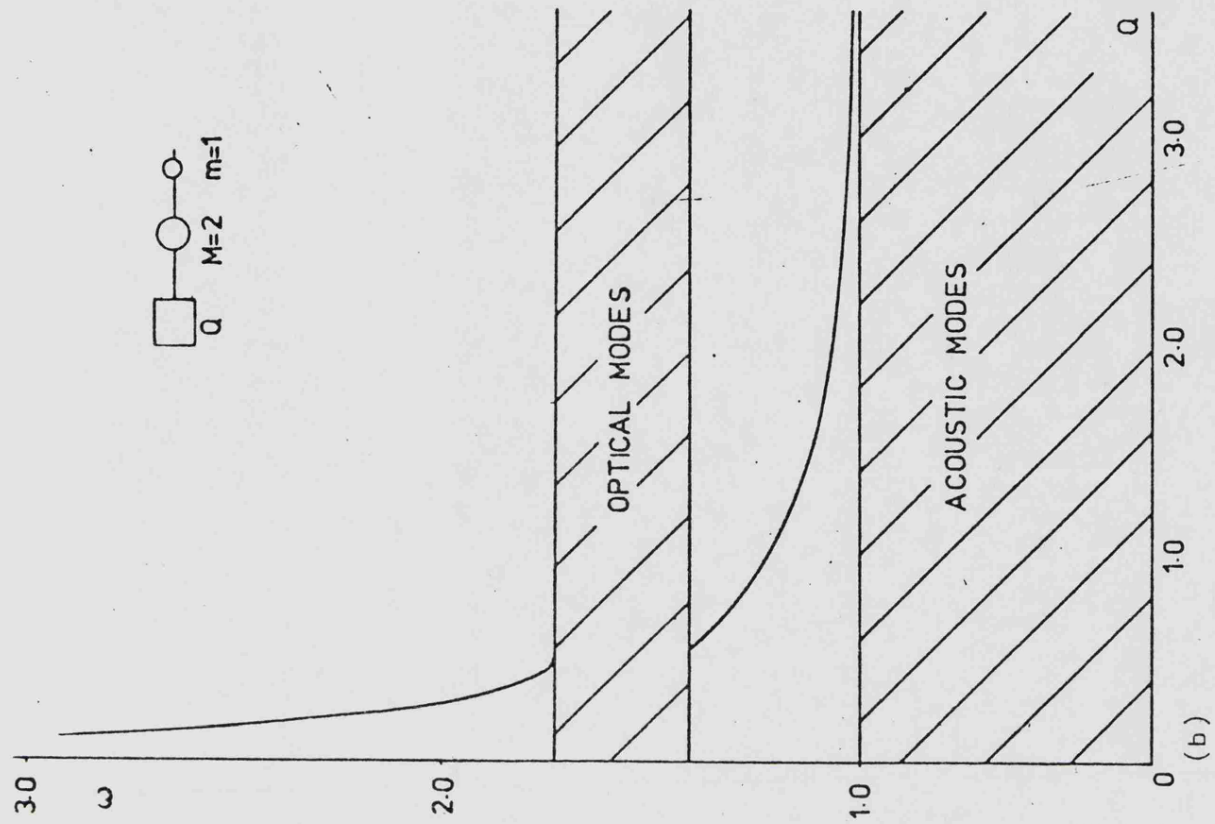
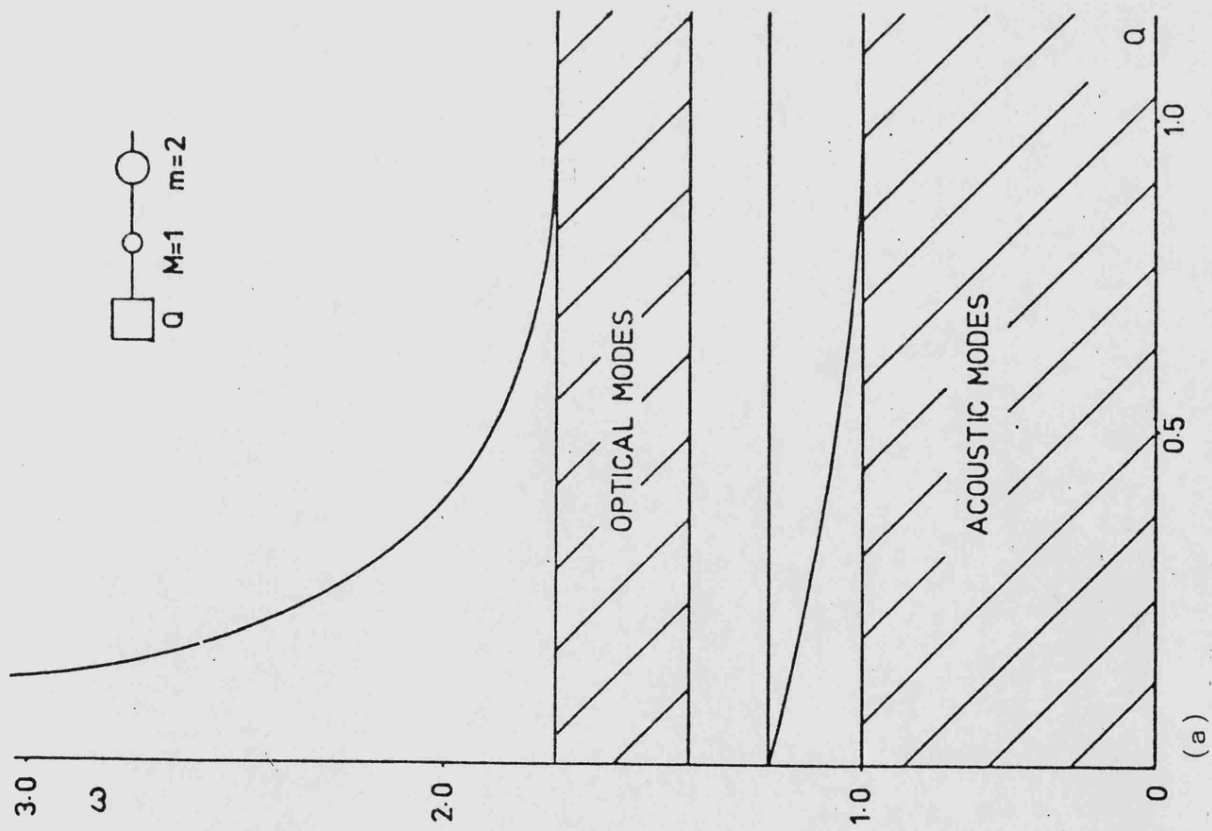


Figure 11.2 The frequency distribution of a diatomic chain with an adsorbed impurity

It is thus possible to evaluate relative amplitudes and modal frequencies for any system of masses harmonically coupled. It will now be shown how such information can be used in studies of atomic desorption.

c) One-dimensional desorption.

In chapter I the concepts of adsorption and desorption were introduced. For an atom to adsorb or desorb from a surface, a relatively large amount of energy must be transferred in a short time. The mechanism describing this process has been frequently studied, however, no basic physical understanding yet exists to explain the phenomena.

In 1936 Lennard Jones and co-workers published a series of papers describing the interaction of atoms with surfaces (27, 28). All but one of these were quantum mechanical; however, the one classical paper (29) discussed the dispersal of energy from an activated link using a stationary infinite harmonically coupled chain to represent the system. When one atom was set in motion, the rate at which energy was dissipated along the chain was discussed in terms of an adsorbed atom being de-activated from a higher to a lower vibrational state. The model was revived independently by Cabrera (30) and Zwanzig (31) in 1959 when both attempted to calculate the rate at which energy could be removed from an atom incident upon a stationary surface. Both demonstrated that large amounts of energy could be transferred to a solid by the creation of many phonons. To overcome the limitations of a stationary (cold) surface, Zwanzig proposed that the model could be generalised to include thermal effects in the solid by using techniques similar to those employed by Slater (32) in his theory of unimolecular reaction rates.

Slater modelled a gas of diatomic molecules by an assembly of classically vibrating systems, dissociation occurring when the separation of the atoms reached a critically high value. The unimolecular velocity constant at a temperature T is given by

$$K = \nu \exp - \frac{E_0}{k_B T} \quad (2.13)$$

where ν is a frequency factor, E_0 is the dissociation energy and k_B is Boltzmanns constant. If the interaction potential between two atoms of masses M and m in a diatomic molecule is a cut off harmonic (figure II.3) then the frequency factor is given by

$$\nu = \frac{1}{2\pi} \sqrt{K \left[\frac{1}{m} + \frac{1}{M} \right]} \quad (2.14)$$

where K is the harmonic coupling constant.

In 1966 Goodman (33) proposed a one-dimensional theory of desorption combining the model of Zwanzig with the formalism of Slater. A monatomic chain with near neighbour harmonic coupling represented the substrate. An impurity atom with mass M was coupled via a cut off harmonic potential of strength K to the end atom in the chain of mass m . The lattice had an initial thermal distribution and when the relative separation of the impurity and end atom reached a critical value, R_c , then the impurity had desorbed. Goodman calculated the rate at which atoms desorbed for this system and obtained an expression

$$K_0 = \nu_0 \exp - \frac{E_0}{k_B T} \quad (2.15)$$

where

$$\nu_0 = \frac{1}{2\pi} \sqrt{K \left[\frac{1}{m} + \frac{1}{M} \right]}$$

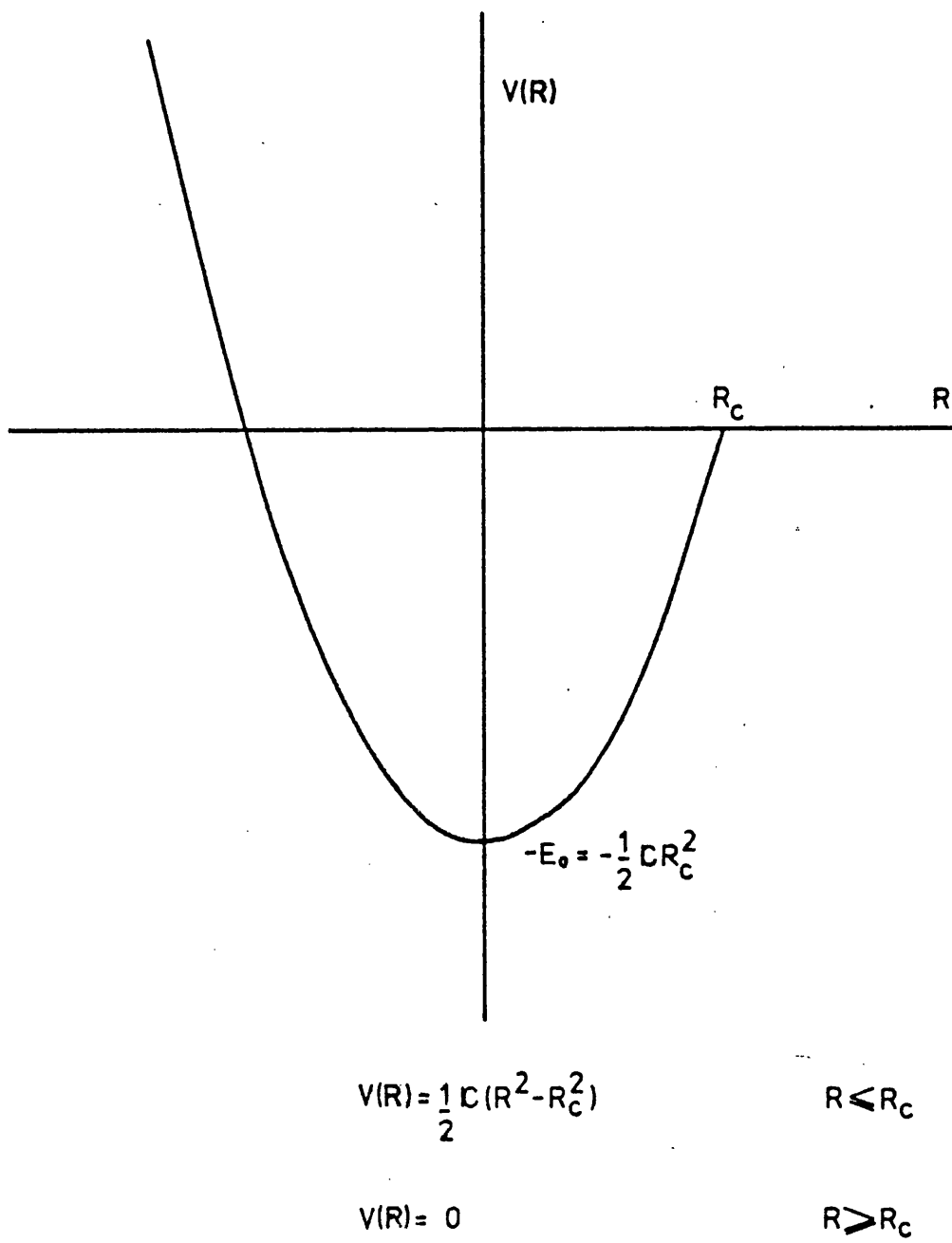


Figure II.3 The cut-off harmonic potential.

Here K_0 is simply the reciprocal of the surface delay time, τ .

The result suggests that the effects of the coupling of the adsorbed atom to the entire lattice may be replaced by the coupling to a single active centre which interacts with the adatom via an harmonic potential.

A calculation by Beeby and Dobrzynski (34) investigated the scattering of an atom from a surface using the same model. The paper also solved the equations of motion for a monatomic chain and derived an expression for the rate of desorption in terms of a summation over the modal frequencies ω_α of the lattice, weighted by the relative separation of the outermost pair of atoms when in that mode.

$$v_0 = \frac{1}{2\pi} \sum_{\alpha} (\chi_2^{\alpha} - \chi_1^{\alpha})^2 \omega_{\alpha}^2 \quad (2.16)$$

Here χ^{α} is the orthonormal set of modal displacements. The exponent was again the minimum energy required to release the desorbing atom from the potential minimum.

It is relatively simple to reconcile the result of Beeby and Dobrzynski with that of Slater by a more general matrix treatment of the problem (Appendix 1). Consider a perfectly general substrate of N different atoms harmonically coupled in one dimension. The desorbing atom interacts with the substrate by a cut-off harmonic potential to the last atom in the chain. The equations of motion may be written in matrix form

$$M \ddot{\lambda} = -K \lambda \quad (2.17)$$

where $\underline{M}$ is a diagonal matrix the first element of which is the mass M of the desorbing atom and the remaining elements m_i the masses of the substrate atoms. $\underline{K}$ is the force constant matrix given by

$$\underline{K} = \begin{bmatrix} K_{12} & -K_{12} & & & \\ -K_{12} & [K_{12} + \sum_{i=3}^N K_{2i}] & -K_{23} & & \\ & -K_{23} & \ddots & \ddots & \\ & & \ddots & \ddots & \ddots \end{bmatrix} \quad (2.18)$$

and $\underline{\lambda}$ is a vector consisting of the displacements of the atoms from equilibrium. When solving for modal solutions it is usual to rewrite the matrix equation in the standard eigenvalue form

$$[\underline{1} \omega_\alpha^2 - \underline{M}^{-\frac{1}{2}} \underline{K} \underline{M}^{-\frac{1}{2}}] \underline{\chi}^\alpha = \underline{0} \quad (2.19)$$

The mode α has a frequency ω_α and the set of vectors $\underline{\chi}^\alpha$ are orthonormal. The total energy of the system is

$$E = \frac{1}{2} [\dot{\underline{\lambda}}^\dagger \underline{M} \dot{\underline{\lambda}} + \underline{\lambda}^\dagger \underline{K} \underline{\lambda}] \quad (2.20)$$

The general displacement λ_i of the i^{th} atom may be expressed as a sum over the modes of the modal displacements $\underline{\chi}^\alpha$.

$$\lambda_i = \sum_\alpha A^\alpha \chi_i^\alpha m_i^{-\frac{1}{2}} \cos(\omega_\alpha t - \phi_\alpha) \quad (2.21)$$

where the normalised probability distribution of the α^{th} mode is given by

$$P(A^*) dA^{*2} = \frac{\omega_a^2}{2k_B T} \exp \left[-\frac{(A^* \omega_a)^2}{2k_B T} \right] dA^{*2} \quad (2.22)$$

T being the temperature of the system. If the probability of finding the desorbing atom with separation R_c from the active site with velocity R is $P(R_c, \dot{R})$ then from Beeby and Dobrzynski the rate of desorption is given by

$$\tau = \int_0^\infty d\dot{R} \dot{R} P(R_c, \dot{R}) \quad (2.23)$$

where each particle with the critical separation R_c is counted as being desorbed regardless of its velocity. From this point on the desorbing particle is in field free space and will consequently register in the detector. In appendix I it is clearly shown how, when evaluating the thermal averages of $P(R_c, \dot{R})$, the value of the summation in equation (2.16), obtained by Beeby and Dobrzynski, may be performed exactly to give:

$$\sum_a (\chi_2^a - \chi_1^a)^2 \omega_a^2 = \kappa \left[\frac{1}{m} + \frac{1}{M} \right] = \frac{\kappa}{\mu} \quad (2.24)$$

where μ is the reduced mass of the active site - adatom pair.

By substituting this result into equation (2.16), the pre-exponent is identical with the result of Goodman (equation 2.15) and the treatment of Beeby and Dobrzynski is thus reconciled with that of Slater.

d) Conclusions

It is of interest to reflect upon the modal solutions found in the early part of this chapter. It has been clearly shown that with the inclusion of a free surface in a lattice, evanescent

modes of vibration may exist that give rise to large oscillations at the surface. It has further been suggested (25) that these modes play an important part in the energy exchange process between a gas-atom and a solid surface. The strong atom-surface coupling via this mode should therefore be expected to appear in the evaluation of the desorption rate. When evaluating this quantity however it is seen that the only term dependent upon the frequency distribution is the summation in equation (2.24). The exact result obtained for the summation implies that the surface modes do not dominate the desorption process. For a realistic system there is no dominant term in the summation as there are a sufficiently high number of bulk modes which tend to reduce the significance of the surface modes.

Chapter III

THE THEORY OF DESORPTION

a) Introduction

In this chapter the development to three dimensions of the one dimensional model discussed in chapter II is presented, and the theory of desorption from a more realistic potential formulated.

Although the one dimensional model gives a certain amount of insight into the desorption mechanism, its use is limited. From the various forces acting upon a gas atom when near a surface, it is quite clear that motion parallel to the surface may be of great importance. For example, if an incident atom loses only part of its initial energy after interacting with a surface, it is possible for it to migrate across the surface while still confined within the surface potential well (35). Unfortunately, using the one dimensional model, the incorporation of such motion is impossible. Consequently it would be most desirable to extend the one dimensional theory of desorption in chapter II to three dimensions so that such effects may be included.

In this chapter reference will be made to appendices I and II, where a more detailed discussion of the formulation may be found. Unfortunately, the rate of desorption calculated therein is that measured in the frame of reference of the active centre whereas to permit comparison with experiment, the rate of desorption needs to be calculated in the frame of reference of the detector. The calculation presented hereafter follows that of the appendices, the only significant modification for the change of reference frame being that, in the final expression for the rate of desorption, the actual mass of the adatom replaces the reduced mass of the adatom-active site pair (36).

b) Three dimensional desorption within the harmonic approximation

The substrate is a perfectly general lattice within the harmonic approximation. For calculational purposes consider a monatomic lattice with central forces only; a more general discussion is presented in appendix 1. As only central forces act it is possible to decouple the lattice into three mutually orthogonal one-dimensional chains, each containing the active centre as a constituent atom (figure III.1(a)). The normal modes of vibration may therefore be calculated in precisely the same way as was done for the one-dimensional lattice. The displacement of the adatom with respect to the active centre is given by

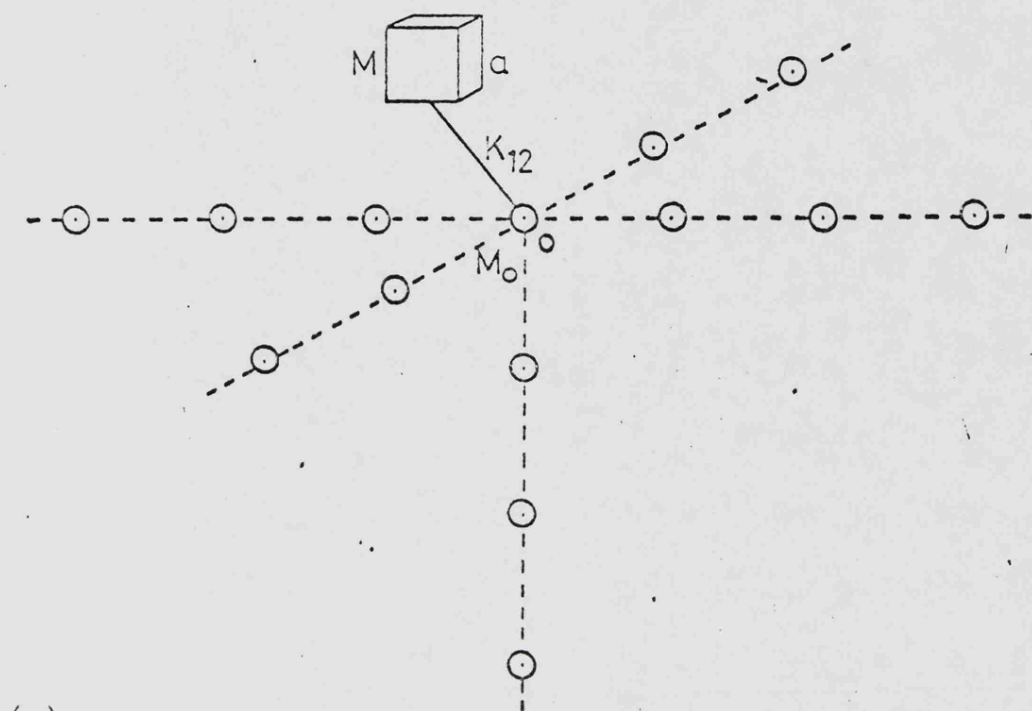
$$r_e = \sum_{\alpha} A_{e}^{\alpha} [\chi_{\alpha,e}^* M^{-\frac{1}{2}} - \chi_{\alpha,e}^{\alpha} m_0^{-\frac{1}{2}}] \cos(\omega_{\alpha,e} t - \phi_{\alpha,e}) \quad (3.1)$$

As in one dimension the amplitudes A_e^{α} are given by a Maxwell Boltzmann distribution and the phases $\phi_{\alpha,e}$ are undetermined. M is the mass of the adatom and m_0 the mass of the active centre, χ_e^{α} is the orthonormal set of modal displacements. The summation is over the modal frequencies α and e runs over the directions x, y, z .

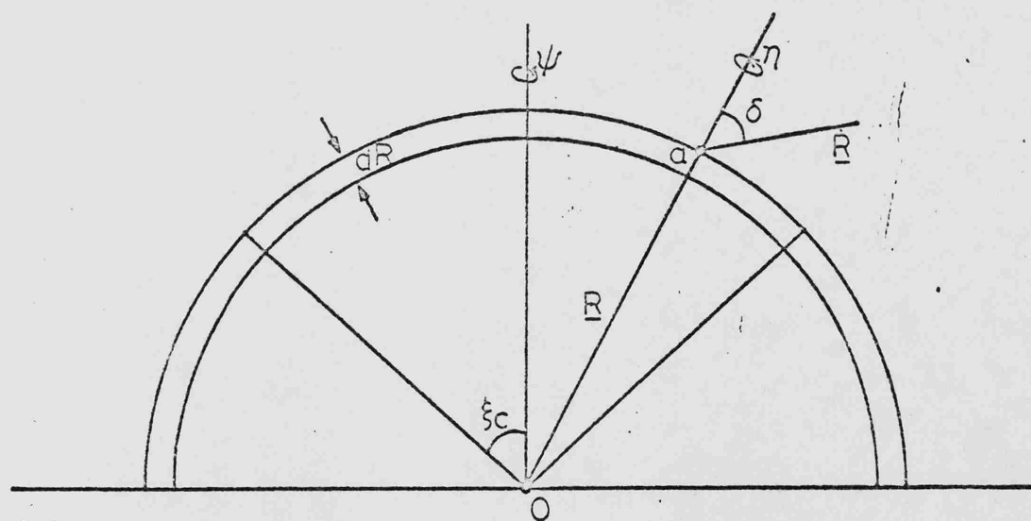
In one dimension, equation (2.23) gave the rate of desorption for the system. In three dimensions this expression requires certain modifications to account for the physical restrictions. Placed upon the desorbing atom, figure (III.1(b)) illustrates the coordinate systems chosen. The position and velocity of the adatom with respect to the active centre is given by

$$\begin{aligned} \underline{R} &= (R, \xi, \psi) \\ \dot{\underline{R}} &= (\dot{R}, \delta, \eta) \end{aligned} \quad (3.2)$$

The rate of desorption is given by



(a)



(b)

Figure III.1 (a) Illustration of the three perpendicular chains used in the harmonic desorption calculation.
 (b) Illustration of the spherical harmonics defined by equation (3.2)

$$Z^{-1} = \int d\underline{\dot{R}} \, R_c^2 \sin \xi \, d\xi \, d\psi \, \hat{\underline{R}} \cdot \underline{\dot{R}} \, P(\underline{R}_c, \underline{\dot{R}}) \\ \times \Theta(\underline{R} \cdot \underline{\dot{R}}) \Theta(\xi_c - \xi) \quad (3.3)$$

where $\Theta(x)$ is a Heaviside step function defined by

$$\begin{aligned} \Theta(x) &= 0 & x < 0 \\ \Theta(x) &= 1 & x > 0 \end{aligned} \quad (3.4)$$

$$\dot{\Theta}(x) = \delta(x)$$

In this expression $R_c^2 \sin \xi \, d\xi \, d\psi$ is the real space volume element and the term $\underline{R} \cdot \underline{\dot{R}}$ ensures that the rate calculated includes only those particles travelling away from the active centre (see figure III.1(b)). $\Theta(\underline{R} \cdot \underline{\dot{R}})$ restricts the limits of integration to include only those particles which have a positive component of momentum in a direction normal to the surface. Clearly particles not satisfying this criterion will never be free of the surface potential. The second theta function $\Theta(\xi_c - \xi)$ restricts the angular limits of integration to include only those particles that are within a polar angle ξ_c to the surface normal drawn through the active site. To determine ξ_c one imagines a crystal surface to consist of an array of atoms, each one being an active site for desorption, then, by constructing a sphere of radius R_c about each site, one obtains a highly complex surface above which the potential vanishes. Such a surface may be divided up into unit cells about each active centre and the part of the sphere associated with each unit cell will determine the limits of angular integration of ξ and ψ . The Θ -function therefore approximates such a surface by a spherical cap above each active site through which the atoms can

desorb; atoms with trajectories not satisfying this criterion are counted as remaining trapped. The final term in the expression is $P(\underline{R}_c, \dot{\underline{R}})$ and as before in one dimension this is the probability of finding the adatom at position $\underline{R}_c$ with velocity $\dot{\underline{R}}$ with respect to the active site.

This expression includes some particles in the desorbing flux which possibly could have hopped into the sphere of influence of an adjacent site. If, however, the atoms upon the surface are in a statistical equilibrium then an equal number of atoms will hop into an active region as out of it and consequently the rate determined by equation (3.3) will be correct.

The probability function is easily evaluated from:

$$P(\underline{R}, \dot{\underline{R}}) = \langle \delta(\underline{R} - \underline{r}) \delta(\dot{\underline{R}} - \dot{\underline{r}}) \rangle \quad (3.5)$$

where the Dirac brackets denote an average over a thermal ensemble. As the lattice may be effectively decoupled the full three-dimensional probability function may be expressed as a product of three one-dimensional distributions.

$$P(\underline{R}, \dot{\underline{R}}) = \prod_{\epsilon=1}^3 \int d\underline{r} d\underline{\dot{r}} P(r_{\epsilon}, \dot{r}_{\epsilon}) \delta(\underline{R} - \underline{r}) \delta(\dot{\underline{R}} - \dot{\underline{r}}) \quad (3.6)$$

where $\underline{r} = (r_x, r_y, r_z)$

$\dot{\underline{r}} = (\dot{r}_x, \dot{r}_y, \dot{r}_z)$

A formal derivation of $P(\underline{R}, \dot{\underline{R}})$ is given in appendix II which on substitution into equation (3.3) gives

$$\tau = \frac{\pi k_B T}{E} \sqrt{\frac{M}{k_{12}}} \frac{1}{(1 - C_0 \xi_c)} \exp \frac{E_0}{k_B T} \quad (3.7)$$

Again the desorption energy is given by the energy required to escape from the harmonic minimum. One noticeable difference from the one-dimensional result is the appearance of both the desorption energy and the surface temperature in the pre-exponential factor.

c) Desorption from a General Potential

The above derivation of the surface residence time, is for an atom interacting with a single active site in the surface via a cut off harmonic potential. Although the general form of this potential satisfies the gross requirements of the gas-solid interaction described in chapter 1, to decouple in the three-dimensional calculations, it was necessary for the potential minimum to be located on the surface active site. Realistically this would be quite impossible due to the finite size of atoms. Moreover a real potential would not abruptly rise to zero at some fixed distance from the surface but would gradually approach zero as indicated in figure (I.1). Finally the electron overlaps at small separations from the surface would give rise to a very hard repulsive interaction and not the "soft" form which is modelled by a quadratic term in the harmonic potential. Generally, therefore, the cut-off harmonic potential does not model the atom-surface interaction in a very realistic manner. Consequently, before comparison with experimental results is possible, the delay time should be calculated for a potential that more accurately describes the interaction.

The technique for calculating the rate of desorption used in the previous section rests upon evaluating the rate at which atoms pass through an imaginary barrier at a distance R_c from the active centre. At this separation the gas-surface pair potential is zero.

For the same conditions to be applicable for a realistic interaction potential, the critical separation R_c would have to be very large to account for the gradual decay of the potential. This seriously affects the desorption rate, as the rate of atoms passing this barrier will now be extremely low, for during the total interaction time the atom will be predominantly located in the region of small potential.

This problem has been studied by Jewsbury and Beeby (37) who have formulated a desorption rate for a general potential in one dimension. To count the atoms desorbing, a barrier is supposed to be placed at a distance, x_c , from the surface where the potential is very small. The rate at which atoms strike this barrier is again given by

$$R = - \int_{-\infty}^{\infty} dv \, v \, P(x_c, v) \quad (3.8)$$

Instead of solving the equations of motion however the evaluation of $P(x_c, v)$ was performed by a statistical thermodynamic approach. This technique enabled a solution to be evaluated for any general gas-solid pair potential. An essential difference of this calculation to that already presented is that the calculated rate R is not equal to the desorption rate. The average time R^{-1} for an atom introduced into the system to emerge after interacting with the surface, is composed of two parts: the time actually spent by the atom interacting strongly with the surface, τ , and the time, t_0 , spent by the atom traversing the region of weak potential. Consequently the measured desorption lifetime is given by

$$\tau = R^{-1} - t_0 \quad (3.9)$$

This type of correction is well known in the experimental scattering of atoms from surfaces, where to define an interaction time at the surface, flight times must be subtracted from the total measured times (38). The mathematical derivation of the surface delay time will now be given.

A one-dimensional lattice consists of N particles interacting via near neighbour potentials $V_i(x_{i+1} - x_i)$. Suppose at some arbitrary time an atom is introduced into the system at the barrier, placed at a distance x_e from the end atom. The total time taken to interact with the surface and return to the barrier is given by R^{-1} . To maintain an equilibrium distribution inside the system, the barrier is supposed to be infinitely repulsive and consequently the atom is elastically reflected, thus conserving the number of particles in the system. The total energy of the system is given by

$$E = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + V_1(x_1 - x_2) + \sum_{i=3}^N \left[\frac{1}{2} m_i v_i^2 + V_i(x_{i+1} - x_i) \right] \quad (3.10)$$

and for a large number, N , of particles of masses m_i at positions x_i : with velocities v_i , $P(x_e, v)$ can be evaluated from

$$P(x_e, v) = \frac{\int \delta(x_1 - x_2 - x_e) \delta(v_1 - v_2 - v) e^{-E/k_B T} \prod_{i=1}^N dx_i dv_i}{\int e^{-E/k_B T} \prod_{i=1}^N dx_i dv_i} \quad (3.11)$$

By substitution from equation (3.10) into (3.11):

$$P(x_e, v) = \frac{\exp \left[-\left(\frac{1}{2} m_1 v^2 + V_1(x_e) \right) / k_B T \right]}{\int dx dv \exp \left[-\left(\frac{1}{2} m_1 v^2 + V_1(x) \right) / k_B T \right]} \quad (3.12)$$

which when substituted into equation (3.8) gives

$$R = \frac{\sqrt{\frac{k_B T}{2\pi m_1}} \exp[-V_1(x_c)/k_B T]}{\int_{-\infty}^{x_c} dx \exp[-V_1(x)/k_B T]} \quad (3.13)$$

In order to evaluate the residence time, a value for the transit time, t_0 , must be obtained. This is the time taken for an atom to traverse the distance from the barrier at x_c to the region of strong potential and back again. Suppose that the incident beam is at the same temperature as the surface and that accommodation is complete, then

$$t_0 \approx 2(x_c - d) \int_0^\infty \frac{1}{v} MB(v) dv \quad (3.14)$$

where $MB(v)$ is the normalised Maxwell Boltzman velocity distribution for a beam of atoms and d is the position of the potential minimum.

On evaluation

$$t_0 \approx \sqrt{\frac{2\pi m_1}{k_B T}} (x_c - d) \quad (3.15)$$

and the surface delay time is

$$\tau = \sqrt{\frac{2\pi m_1}{k_B T}} \int_0^{x_c} [e^{-V(x)/k_B T} - \Theta(x-d)] dx \quad (3.16)$$

In Practice it is normal to take the limit of $x_c \rightarrow \infty$, as the dominant behaviour of this expression is due to the potential minimum.

In appendix II it is shown how the one dimensional cut-off harmonic result can be obtained by this type of analysis and how the delay time can be evaluated for a three dimensional system when the gas-surface potential is perfectly general.

A complete description of the generalization to three dimensions is presented in appendix II. Each desorbing atom has an extra degree of freedom, which is parallel to the surface. Suppose there to be associated with each surface active site a Wigner Seitz area defined by

$$\pi r_s^2 = \rho_s^{-1} \quad (3.17)$$

where ρ_s is the density of surface active sites. The volume into which the particle is introduced is defined by the extension of this boundary up to some fixed height. Only when an atom strikes the top of the barrier is it counted as being desorbed and consequently reintroduced into the system. If the atom strikes the side walls then this may be considered as an equilibrium exchange of atoms between neighbouring surface sites. Suppose the barrier is at a distance r_c from the surface atom. The rate of striking the barrier is given by

$$R = \int d\underline{r} \quad \underline{\hat{r}} \cdot \underline{\hat{r}} \Theta(r, \underline{\hat{r}}) \Theta(\xi_c - \xi) P(r_c, \underline{\hat{r}}) \quad (3.18)$$

where each term has its counterpart in equation (3.3) for the harmonic analysis. On evaluation of $P(r_c, \underline{\hat{r}})$ by substitution of a Maxwell Boltzman surface distribution, each of the terms involving the bulk atoms cancel, leaving a two-body expression as in equation (3.12).

$$\frac{1}{R} = \sqrt{\frac{m_i}{2\pi k_B T}} \frac{\int d\underline{r} e^{-V(r)/k_B T}}{2 r_c^2 (1 - \cos \xi_c)} \quad (3.19)$$

Using this result the delay time is given by

$$\tau = \frac{1}{v_{ws}^2} \sqrt{\frac{m_i}{2\pi k_B T}} \int dr e^{-V(r)/k_B T} - t_0 \quad (3.20)$$

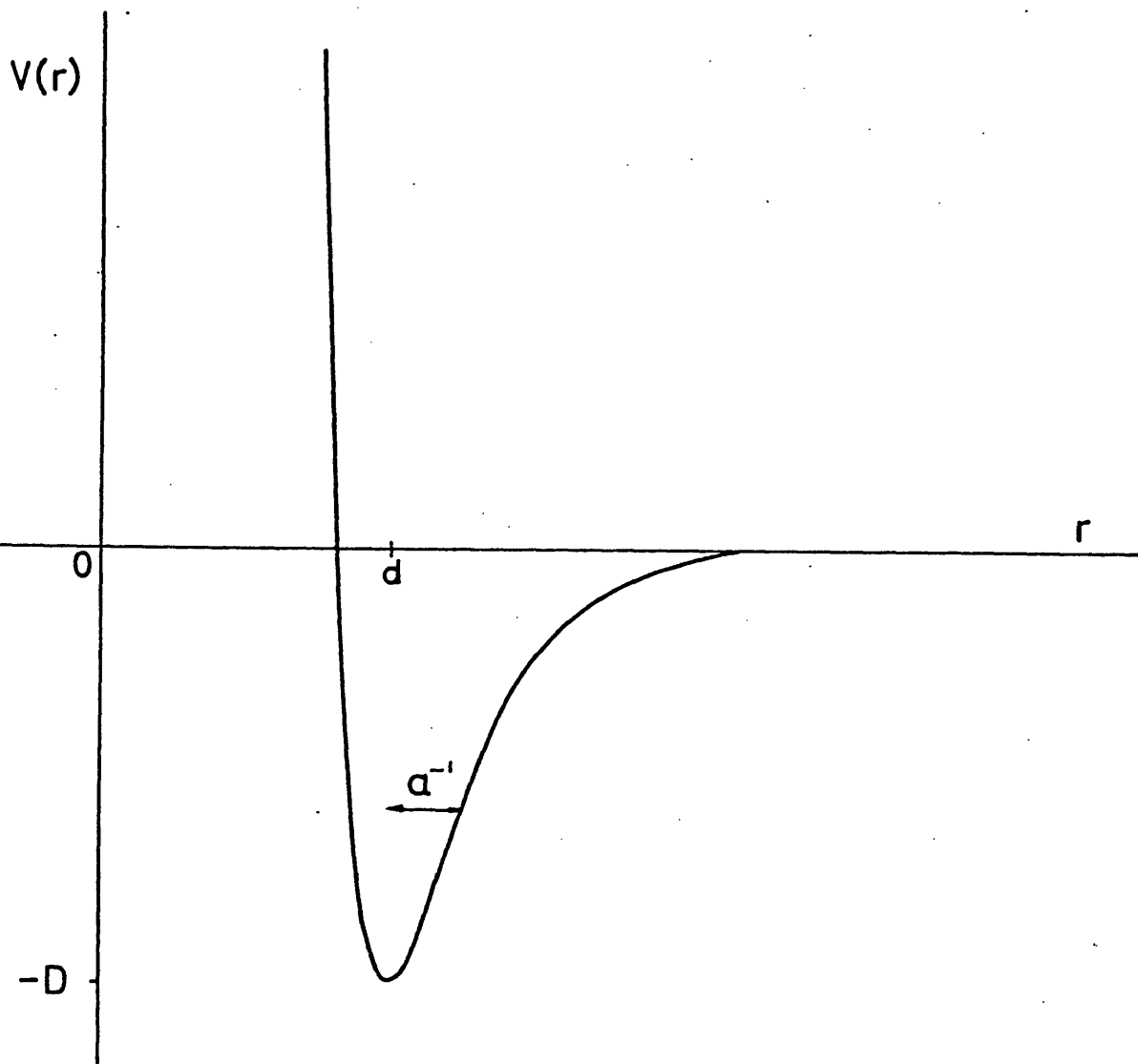
The value of t_0 is obtained simply by putting $V(\underline{r}) = 0$ in equation (3.19) which approximates the transit through the weak potential as being the time taken to cross field-free space. The final expression for the surface delay time is therefore

$$\tau = \frac{1}{v_{ws}^2} \sqrt{\frac{m_i}{2\pi k_B T}} \int dr \left[\exp\left(-\frac{V(r)}{k_B T}\right) - 1 \right] \quad (3.21)$$

The form of pair potential chosen will obviously affect the calculated surface delay time. In order to permit a comparison with experimental results, various forms of potential will be used in order to model various geometrical surface features. The basic form of pair potential chosen in these calculations is the Morse Potential which is illustrated in figure III.2 (27).

$$V_i(r) = D \left\{ \exp[-2(r-d)a] - 2\exp[-(r-d)a] \right\} \quad (3.22)$$

where D is the depth of the attractive well, a is an inverse length parameter which is related to the half-width of the potential and d is the position of the potential minimum. The potential has a short range repulsive part plus a long range exponential attraction which slowly decays at distances remote from the surface. The major advantage of using a Morse potential over using a two parameter Lennard Jones potential, is the extra degree of flexibility obtained which enables overlayer spacings that are different from bulk near neighbour separations.



$$V(r) = D \left[e^{-2(r-d)a} - 2e^{-(r-d)a} \right]$$

Figure III.2 The Morse Potential

d) Comparison with experiment

Experimentally the two measurable quantities associated with desorption (τ_0, D) are deduced by plotting the surface delay time as a function of the inverse temperature. The potential chosen to represent this interaction has three parameters (a, d, D) and consequently when making a computational comparison with an experiment, a series of values of a and d may be fitted to the results. The range of these values may be limited by simple arguments, for example it would be extremely unlikely for the adatom to be situated further than two or three lattice spacings from the surface; but for a detailed understanding of the interaction a second experiment must be performed, preferably within the same vacuum system, to determine either d or a . Possible experiments include low energy ion scattering (39) which may determine the overlayer spacing, d , as can low energy electron diffraction (40) once a thorough computational analysis is performed. Alternatively, for a diffracting system, using selective adsorption (2) a value for both the potential width and depth may be found with the consequential determination of the overlayer spacing.

Flash desorption is the most common technique appearing in the literature for evaluating the pre-exponent, τ_0 , and the desorption energy D . Experimentally the technique is relatively simple in that an amount of gas is adsorbed onto a cold solid surface within a vacuum system. A temperature programmed ramp is applied to the sample and the pressure change monitored. By very careful examination of the data it is possible to evaluate both τ_0 and D as a function of initial coverage (41). The theoretical analysis presented in this chapter however becomes cumbersome when adatom-adatom interactions cannot be neglected and consequently flash desorption data can only be utilised for deducing potential parameters if the initial coverage is less than 10^{-3} of a monolayer.

A second technique is that of Molecular Beam Relaxation Spectroscopy (42). A modulated thermal beam of atoms impinge upon a substrate where they interact with the surface potential field; the desorbed flux is then synchronously detected with respect to the modulation. Schematically this is shown in figure III.3. The desorbed flux has a definite phase and amplitude which, when compared with the incident beam, can provide information on the processes occurring at the surface. Typical beam fluxes for such an experiment are of the order of 10^{12} atoms/sq.cm/sec and when in equilibrium will act as only a small perturbation on the surface. Any adatom-adatom interactions are unlikely to be important and consequently data from such experiments are a better test for this theory.

The available data falls broadly into three categories:

- a) ions and atoms interacting with polycrystalline tungsten;
 - b) metal atoms interacting with polycrystalline tungsten;
 - c) type III atoms interacting with semiconductor single crystals.
- a) The study of alkali atoms and ions with surfaces covers the longest time span. The earliest experiments date back to 1933 when Evans (43) investigated the desorption of potassium ions from polycrystalline tungsten surfaces. This system has subsequently been studied by Knauer (44) in 1948, Popp (45) in 1964, Kaminsky (46) in 1966, and more recently by Smith et al (47) in 1970 and Isa et al (48) in 1974, and the data is set out in Table III.1. For an analysis of problems encountered in the earlier experiments and a full discussion of the various values the reader is referred to the paper by Smith et al (47). From this work it seems that the values pertaining to the clean system are $\phi_0 = 2.4 \times 10^{-13}$ and $D = 2.36$ eV. It is very interesting to observe that on contamination of the surface by carbon, D remains constant but ϕ_0 is reduced. It is not at all clear what

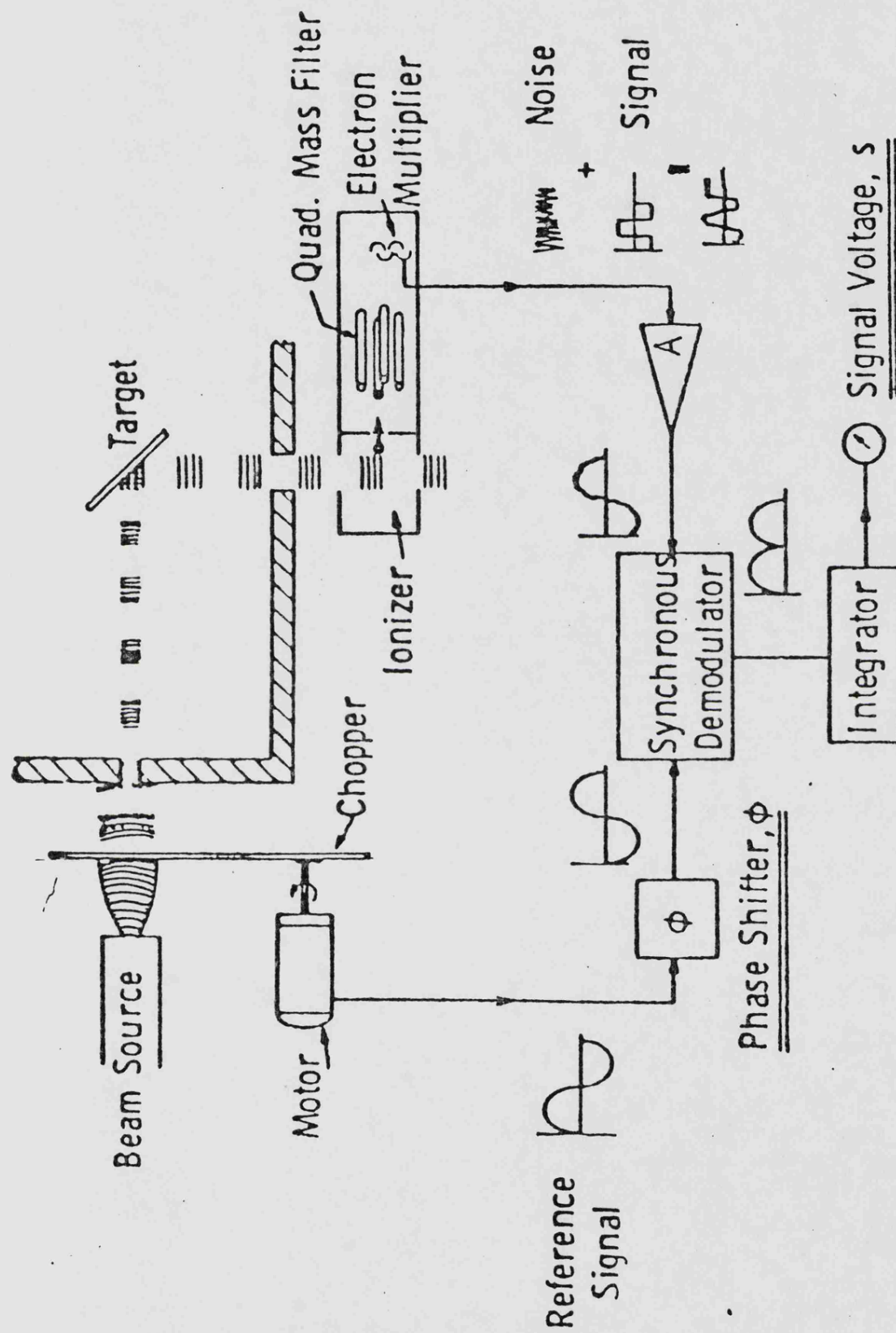


Figure III.3 Schematic of a modulated molecular beam system for the study of gas-surface reactions

causes this reduction in the pre-exponential but it would perhaps be informative to see the results from a similar experiment upon a single crystal sample. It is possible that the high number of grain boundaries found on polycrystalline samples enhance the desorption probability with the consequent reduction of τ_0 . As can be clearly seen from the large spread in values of τ_0 the effect of surface contaminants strongly influences the desorption probability. Due to the great improvement in vacuum techniques, and methods of producing "clean" surfaces, the recent data is assumed to be more reliable. Unfortunately Isa et al (48) had no monitor of surface contamination in their system and their results yield for a sample believed to be clean, a pre-exponential factor which is within a factor of two of the carbonised surface of Smith et al (47). For this reason we have chosen the decarbonised data of Smith et al as representing the interaction between a "clean" surface of polycrystalline tungsten and potassium ions.

To obtain an estimate of potential parameters a value is required for the area of a typical adsorption site upon a polycrystalline tungsten surface. There have been various speculations as to the structure of such surfaces but recent investigations on copper (49) have shown that the adsorption properties are similar to those found on high index faces. On such faces the density of active sites is lower than that on the low index ones and consequently the area of such an adsorption site is larger. By inspection of equation (3.21) it is seen that a larger value of r_{ws} will result in smaller values of the pre-exponential factor τ_0 . For a typical (311) face of tungsten the value of r_{ws} is $3.33 \text{ \AA}$ and this is the value that has been taken for the polycrystalline samples. The bonding to the metal surface is taken as being via a single

<u>System</u>	<u>Reference</u>	<u>τ_0(secs)</u>	<u>D(eV)</u>	<u>$a^{-1}(\text{\AA})$</u>	<u>d(\text{\AA})</u>	<u>Comments</u>
K ⁺ - W	(43)	9.37×10^{-14}	2.43			"Gas covered"
	(44)	2.00×10^{-12}	2.9			"
	(45)	1.75×10^{-13}	1.95			"
	(46)	6.20×10^{-13}	2.30			"Atomically clean"
	(47)	2.40×10^{-13}	2.36	0.98	2.70	"Decarbonised"
	(47)	6.0×10^{-14}	2.36			"Carbonised"
	(48)	3.2×10^{-14}	2.30			"Clean"
Rb ⁺ - W	(43)	2.76×10^{-12}	2.12			"Gas covered"
	(53)	4.0×10^{-12}	2.12			"Essentially clean"
	(46)	1.55×10^{-12}	2.05	3.48	2.85	"Atomically clean"
Cs ⁺ - W	(43)	7.9×10^{-11}	1.80			"Gas covered"
	(44)	4.0×10^{-17}	3.60			"
	(54)	1.1×10^{-12}	2.04	1.78	3.04	"Clean"
	(54)	6.0×10^{-11}	1.55			"Contaminated"
Na ⁺ - W	(46)	8.5×10^{-14}	2.69	0.64	2.35	"Clean"

Table III.1 Experimental values for the residence times of alkali ions on polycrystalline tungsten surfaces, in chronological order, and computed values of the equivalent Morse Potential Parameters.

Morse potential with no direct angular asymmetries. It is thought that, because of the amorphous nature of a polycrystalline metal surface, the ion will be in equilibrium at typically the sum of the hard sphere radii so this is the value chosen for d in each case (50). The results shown in Table III.1 for the half widths of the various ion-metal interactions are rather large and this is thought to be due to the effect of a coulomb attraction at distances far from the surface.

b) The second series of systems chosen for comparison are metal atoms interacting with polycrystalline tungsten surfaces. The experimental data are from two sources and are presented in Table III.2. The data from 1966 by Shelton and Cho (51) yields very small values for the pre-exponential factors when compared to either the rest of the data presented here, or a typical surface oscillation ($\sim 10^{-13}$ sec). For these experiments the vacuum system was evacuated by an oil diffusion pump which in subsequent publications (52) has been criticised as being a possible source of carbon contamination. If these surfaces were carbon contaminated the anomalously low values for the pre-exponentials would agree with the remarks made by Smith et al (47). The data obtained by Cho and Hendricks (52) for noble metals interacting with polycrystalline tungsten yields larger values for the pre-exponential factors and it is interesting to note that in the later experiment the diffusion pump was replaced by an ion pump.

The potential chosen to represent the adsorption site is the sum of four identical Morse potentials, the origin for each potential being the corner of a square with side length $3.16 \text{ \AA}$. The value chosen for the Morse parameter d in the absence of any measured value is taken to be the sum of the hard sphere radii. It

<u>System</u>	<u>Reference</u>	<u>τ_0 (secs)</u>	<u>D (eV)</u>	<u>$a^{-1}(\text{\AA})$ (4x site)</u>	<u>$a^{-1}(\text{\AA})$ (1x site)</u>	<u>d (Å)</u>
Cu - W	(51)	3.9×10^{-14}	3.37	1.85	0.02	2.66
Cr - W		4.5×10^{-15}	4.42	1.10	0.005	2.62
Be - W		2.0×10^{-15}	3.96	1.10	0.005	2.49
Ni - W		3.4×10^{-15}	4.30	0.50	0.005	2.61
Ag - W	(52)	2.7×10^{-13}	2.90	3.00	0.10	2.79
Au - W		1.2×10^{-14}	4.50	1.05	0.005	2.82

Table III.2 Experimental values for the residence times of metal atoms on polycrystalline tungsten surfaces, in chronological order, and computed values of the atom-atom Morse Potential.

is then found that by modelling a highly coordinated site in this way, realistic half-widths of the individual atom-atom Morse potential can be determined. For comparison, computed values for an angular independent single site potential are also shown (Table III.2).

It would be of great interest to obtain more recent data on single crystal samples with which to make a comparison with these results.

c) The third class of systems which we have studied here are group III atoms interacting with semiconductor surfaces and the results are presented in Table III.3. The results of Arthur (10) are discussed at length in appendix II and a reasonable potential obtained. To model the interaction use was made of an angular dependent potential $V(r, \Theta)$ which represented the localisation of electrons in specific directions (dangling bonds) with respect to the surface. The second set of results, from the Grenoble group (55, 56) are for the interactions of indium with single crystal silicon surfaces. Although one might again expect a degree of angular dependence in the interaction, the experimental results may be reproduced by the use of realistic angular independent potentials. As mentioned before no adatom-adatom interactions are considered in the present theory and this could possibly be the reason why any angular dependence is unimportant. In the indium-silicon experiments beam fluxes of 10^{13} - 10^{15} atoms/cm²/sec were used and with such high values the surface would very quickly become indium rich. It is therefore likely that the values of

τ_0 and D measured, refers to an indium rich surface which gives rise to an angular independent interaction. In this calculation it has been assumed that each surface atom is an active site for adsorption and r_{ws} has been calculated accordingly (Table III.3).

System	Reference	τ_0 (secs)	D(eV)	a^{-1} (Å)	d(Å)	r_{ws} (Å)	Incident flux (at/cm ² /sec)
Ga-CaAs (111)	(10)	2.5×10^{-14}	2.47	2.0	2.5	2.96	10^{13}
	(10)	1.6×10^{-14}	2.59	1.4	2.5	2.96	
In-Si	(56)	4×10^{-12}	2.12	3.47	2.79	2.16	
	(56)	4×10^{-13}	2.34	0.26	2.79	1.81	10^{13}
	(55)	8×10^{-13}	2.47	0.23	2.79	1.17	10^{15}

Table III.3 Experimental values for the residence times of group III atoms on semiconductor surfaces and computed values of the equivalent Morse Parameters.

e) Conclusions

The work presented in this chapter plots the development of desorption theory. From an original calculation based upon a one dimensional harmonic model, a quite general theory is formulated which is capable of yielding considerable information about the gas-solid interaction. Comparison with a variety of experimental results are encouraging and justify the approximations made.

Chapter IV

MOLECULAR BEAM EPITAXY

a) Growth Investigation - A Summary

Until recently the fabrication of thin film semiconductor compounds has been limited to either vapour phase epitaxy (VPE) or liquid phase epitaxy (LPE). Both techniques have been widely used in the solid state electronics industry, and many practical devices are manufactured using these methods (57).

Recent advances in the communications industry have given rise to a new generation of solid state devices that operate in the microwave and optical frequency regimes (58). As an example of such a device the Ga As field effect transistor (FET) is chosen to illustrate the stringent requirements placed upon the growth system (59). This device is a low level, low noise microwave amplifier and its basic structure requires a thin n-type epitaxial layer on a semi-insulating substrate. Typically for a structure which operates at 4 GHz, a 5000 Å layer is required with a carrier concentration in the mid $10^{16}/\text{cm}^3$ range. The performance of the device is critically dependent upon the uniformity in both layer thickness and doping profile.

Unfortunately both VPE and LPE suffer from a lack of control for layers of less than one micron, and because of this a new method of growth called Molecular Beam Epitaxy (MBE) has been developed (59,60,61,62). This technique has none of the inherent restrictions of either LPE or VPE with the consequence that precise control over both growth rate and doping profile is possible. An additional feature of MBE is that large area epitaxy is possible, a factor which is of great economical importance. Much of the work

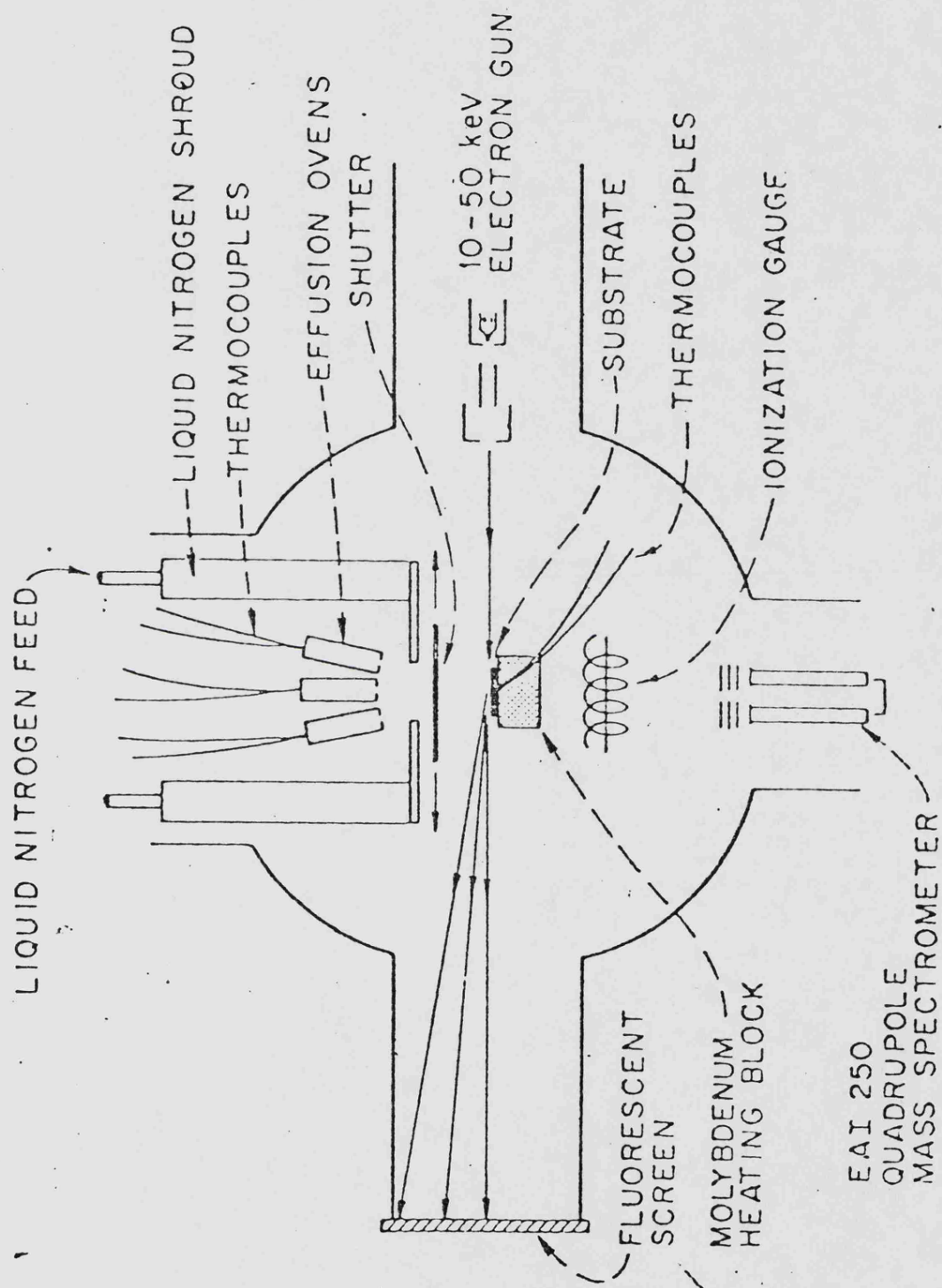


Figure IV.1 Schematic of Molecular Beam Epitaxy growth system

in this field has been concerned with the fabrication of gallium arsenide films and such a system will now be described.

Basically MBE is a very sophisticated form of vacuum evaporation. A heated substrate is bombarded with beams of gallium and arsenic, which originate from individual Knudsen cells (63), the entire construction being in a UHV chamber (figure IV.1). By placing additional cells within the vacuum system it is possible to dope the epitaxial layer during the growth cycle. An argon gun is commonly used for in situ cleaning of the substrate, the final composition of the surface being monitored by both reflection high energy electron diffraction (RHEED) and auger electron spectroscopy (AES). The inclusion of a mass spectrometer in the chamber allows the composition of the molecular beams to be directly monitored.

When elemental gallium is used as a source material in the Knudsen cell, the resulting beam is composed entirely of the monomeric species. For an arsenic beam however there are two source materials in common use: gallium arsenide provides a beam which is predominantly composed of As_2 molecules whereas elemental arsenic produces a beam of As_4 molecules (59).

For GaAs homoepitaxy (i.e. GaAs grown on a GaAs substrate) the primary mechanism controlling the growth rate is the flux of gallium atoms arriving at the surface. At a typical substrate growth temperature of 550°C , gallium atoms have a unit sticking coefficient but the molecular arsenic sticking coefficient is a complex function of the surface topography and the gallium arrival rate (60).

In an attempt to understand the growth mechanism employed by MBE, various kinetic studies have been made (64). In Chapter III for example, results are presented for the residence time of Ga

atoms on a GaAs (111) substrate. More recently Arthur (65) examined the interaction between As_2 molecules and Ga atoms on a GaAs (111) substrate and proposed a semi-quantitative model for the growth mechanism. Foxon and Joyce (64) have made a similar study of the reaction kinetics of As_4 and Ga beams when interacting with a GaAs (100) substrate, and again a model was proposed.

In order to fully explain the kinetic data for the Ga-As-GaAs system, a sound theoretical understanding of molecular desorption is required. In the absence of such a theory, it is possible that a semi-empirical microscopic model for the interaction might provide greater insight into the various processes occurring during the growth cycle and this is the aim of the work presented in this chapter and appendix III. The results from the kinetic study of Foxon and Joyce have been employed, and an alternative model for the interaction of As_4 and Ga beams with a GaAs (100) surface is proposed.

b) Experimental Observations of the Ga- As_4 -{001} GaAs System

The structure of GaAs (100) in the presence of As_2 and Ga beams, has been studied by Cho (66) using (RHEED). Below 500 K or in the presence of an arsenic beam, the symmetry of the surface is $C(2 \times 8)$ and this is generally referred to as being arsenic-stabilized. Alternatively, above 875 K or in the presence of a gallium beam, the surface symmetry is $C(8 \times 2)$ and this is referred to as being gallium-stabilized.

Foxon and Joyce (64) performed a study of the As_4 -Ga-GaAs (100) system over a range of substrate temperatures from 300-900 K. For convenience of presentation their results were discussed in three temperature ranges: 300-450 K, 450-600 K and 600-900 K. The

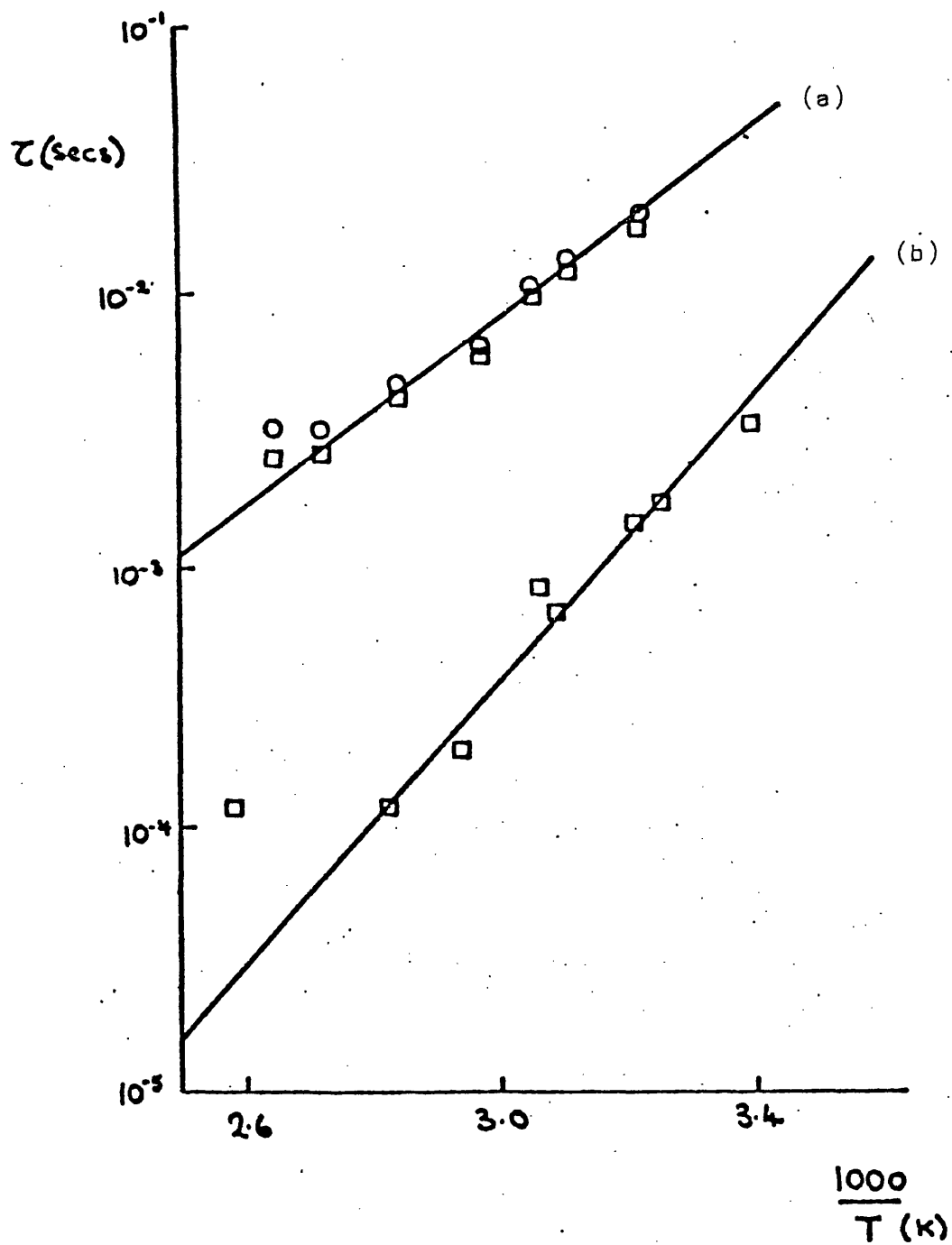


Figure IV.2 Surface Lifetime of As_4 on 100 GaAs surfaces
 (a) Surface Ga-rich
 (b) Surface As-rich

experimental system was in spirit similar to the schematic diagram shown in figure (III.3), the major improvement being the inclusion of a signal-averaging technique in place of the phase sensitive detector (38). This enabled additional information to be obtained on the amplitudes and phases of frequencies other than the fundamental of the output signal.

In the temperature range 300-450 K, the surface delay times of As_4 molecules on gallium-free and gallium-populated surfaces were measured figure (IV.2) . From these data the values of the pre-exponential factors and desorption energies were found:

$$\tau = 9.0 \times 10^{-10} \exp \left[\frac{0.38}{R_g T} \text{ eV} \right] \text{ gallium-free} \quad (4.1)$$

$$\tau = 1.6 \times 10^{-8} \exp \left[\frac{0.36}{R_g T} \text{ eV} \right] \text{ gallium-covered}$$

A certain difficulty was experienced in obtaining reproducible results for the gallium-covered surface as the delay time was found to be critically dependent upon the history of the substrate. These results may be contrasted with the results for atomic delay times presented in Tables (III.1-3). From the analysis presented in Chapter III it is clear that pre-exponentials differing significantly from within two orders of magnitude of 10^{-13} seconds suggest that thermally activated desorption is not the rate limiting process.

In the second temperature regime 450-600 K the sticking coefficient of the As_4 molecules, S , was found to be temperature independent, the sticking coefficient of gallium always being unity. In the absence of any surface gallium, S was found to be zero. However, by simultaneously impinging beams of As_4 and Ga, S took a finite value which showed a linear relationship with the gallium arrival rate up to a value of about one half figure (IV.3) . The reaction

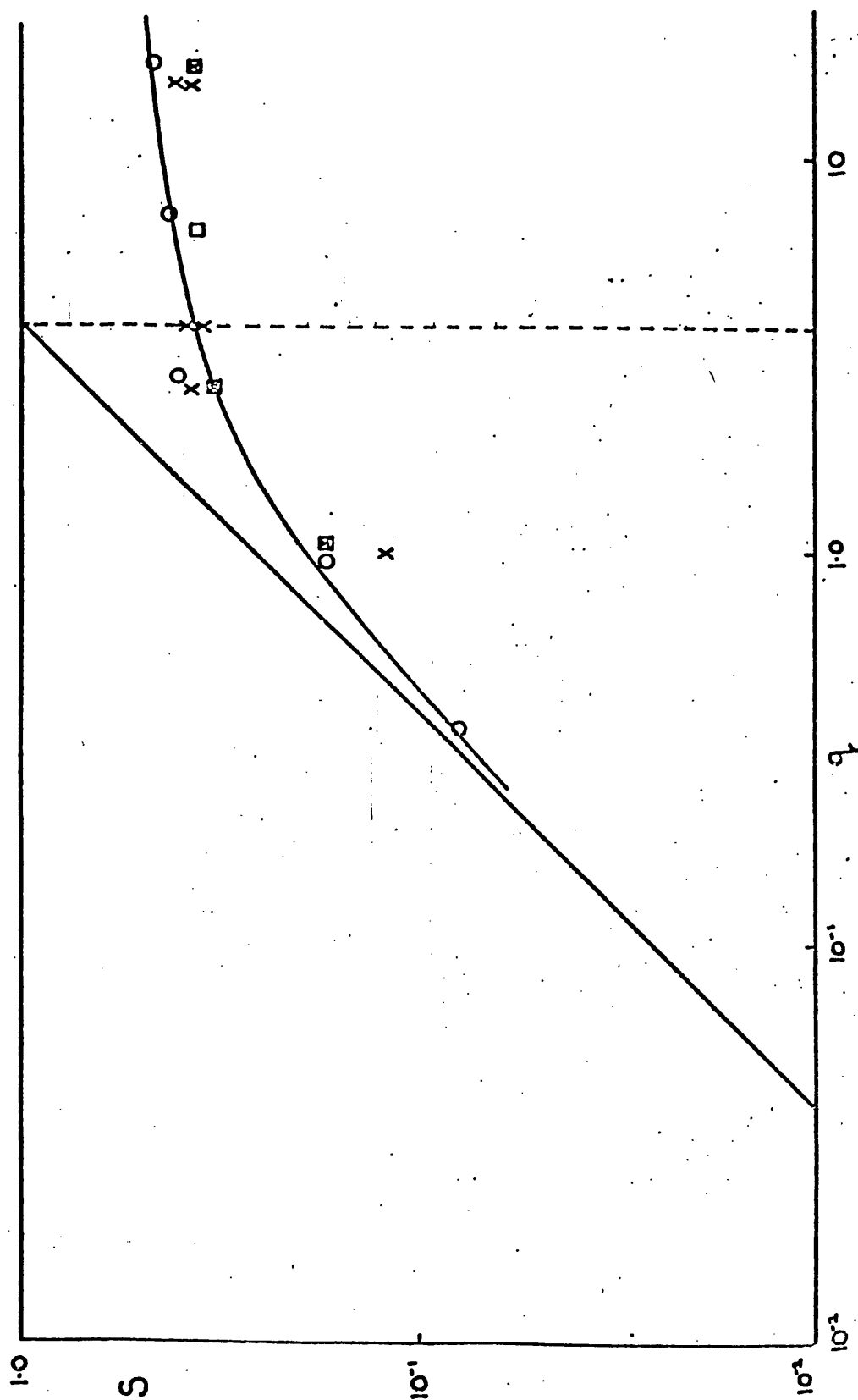


Figure IV.3 The sticking coefficient of As_4 on GaAs as a function of the flux ratio q . The experimental points agree well with the theoretical line; shown also is a one-atom of As to one-atom of Ga sticking line ($S = \frac{1}{4}q$) and the dividing line between excess Ga and As arriving at the surface

order of the As_4 adsorption-desorption process was also measured with respect to the gallium flux. At low arsenic fluxes desorption was found to be second order, the process becoming first order when the arsenic flux was increased. The second order reaction suggests that when the surface is predominantly covered with gallium, there is a direct or indirect interaction between the As_4 molecules (or their fragments) which dominates the desorption process.

c) Surface Events and Model Description

To envisage molecular desorption as being atomic-like in nature is perhaps a gross simplification of the problem. However, as a first approximation, if one supposes the molecule as being rather inert, then the formalism developed in Chapter III may be used to give order of magnitude estimates for desorption parameters.

From equation (3.21) the delay time of an adatom of mass M bound to a substrate via a surface potential $V(\underline{r})$ is

$$\tau = \frac{1}{\Gamma_{\omega_s}^2} \sqrt{\frac{M}{2\pi k_B T}} \int d\underline{r} \left[e^{-V(\underline{r})/k_B T} - 1 \right] \quad (4.2)$$

The desorption is characterised by:

- a) no sticking,
- b) full thermal accommodation,
- c) a first order adsorption-desorption reaction.

These requirements are satisfied in full for the interaction of an As_4 molecule with a gallium free surface. From figure (IV.2), the best fit of a straight line through the points which correspond to an arsenic-stabilized surface gives a value of the delay time:

$$\tau = 3.8 \times 10^{-10} \exp \left[\frac{0.40 \text{ eV}}{k_B T} \right] \quad (4.3)$$

Experimentally, these measurements become less reliable as the substrate temperature is increased and the operational limit of the electronics is approached. For this reason Foxon and Joyce weighted against the higher temperature points and obtained $E = 0.38 \pm .03$ eV. If the highest temperature point is neglected altogether, then the best fit through the remaining points is

$$\tau = 3.85 \times 10^{-12} \exp \left[\frac{0.53 \text{ eV}}{k_B T} \right] \quad (4.4)$$

If the desorption of As_4 molecules from an arsenic-stabilized GaAs (100) surface is pseudo-atomic, then the value of the pre-exponential factor in equation (4.4) would be within the physical bounds previously ascribed to a thermally activated process. On an arsenic stabilized surface the only additional factors affecting the surface delay time are:

- a) fragmentation,
- b) admolecule-admolecule interaction, and
- c) admolecule-surface imperfection interaction.

Experimentally the observation of only As_4 in the desorbing flux and a zero sticking coefficient indicates that (a) is perhaps unlikely. In the experiments, low beam fluxes were purposefully used in an attempt to minimize (b) and the observation of first order kinetics is further evidence that no lateral interaction occurs between admolecules. Consequently only (c) remains as a process which could possibly influence the surface delay time.

When the As_4 flux is low, the surface is gallium stabilized and the pre-exponential as derived from figure (IV.2) is sufficiently outside the range of values set by the atomistic desorption calculation to exclude this as being the rate limiting step. It is not

unreasonable to expect the As_4 molecules to bond more strongly to a gallium site than an arsenic site as the As-As bond is weaker than the As-Ga bond. From the Frenkel equation (1.1) it is known that even a small increase in the binding energy can give rise to a very large increase in the total delay time, with the consequence that an As_4 molecule is unlikely to desorb from a gallium surface site. If an As_4 molecule lands on a gallium rich surface it can:

- 1) hop from site to site,
- 2) dissociate and grow GaAs, or
- 3) desorb.

In the temperature range under consideration (~ 500 K), a typical surface lifetime might be 10^{-2} seconds during which time the dissociation of some As_4 molecules will undoubtedly take place. Thus for all values of the incident arsenic flux, there will be a small fraction of arsenic surface sites, their number being dependent upon that flux. It is proposed that when an As_4 molecule lands upon a gallium stabilized surface, the rate limiting step for desorption is the probability of that molecule finding an arsenic site from which to desorb. On arrival at such a site, the desorption characteristics will be that of the lower curve in figure (IV.2), a time considerably shorter than the upper curve which represents the total surface delay time. This proposition is supported experimentally by the observation of second order reaction kinetics.

d) Mathematical Description

Consider beams of As_4 and Ga incident upon a GaAs (100) surface with fluxes J_{AS} and J_{GA} respectively. When steady state conditions are obtained, a certain fraction of the incident arsenic molecules, S , will stick, the remainder eventually desorbing.

As previously mentioned the sticking coefficient for gallium atoms is unity and hence the rate of destruction of surface arsenic sites is given by $J_{Ga} \Theta_{As}$. Here Θ_{As} is that fraction of the surface which is occupied by arsenic sites. In equilibrium this rate of destruction of sites is equivalent to the rate of creation of arsenic sites, i.e.

$$4 S J_{As} = \Theta_{As} J_{Ga} \quad (4.5)$$

Let p be the fraction of As_4 molecules which survive migration to an arsenic site without being dissociated. Since As_2 is the natural desorbing species from GaAs, any surface recombination is unlikely and so such processes are neglected. If τ_{stick} and $\tau_{migrate}$ are the mean times taken for the As_4 molecule to dissociate, and to migrate to an arsenic site when initially being on a gallium site, then the probability of an As_4 molecule being intact upon a gallium site after t seconds is given by $e^{-t/\tau_{migrate}}$. At this time, the rate of migration per molecule is $e^{-t/\tau_{migrate}} e^{-t/\tau_{stick}} / \tau_{migrate}$, hence

$$p = \int_0^{\infty} \frac{dt}{\tau_{migrate}} \exp -t \left[\frac{1}{\tau_{migrate}} + \frac{1}{\tau_{stick}} \right] \quad (4.6)$$

which after integration

$$p = \frac{\tau_{stick}}{\tau_{migrate} + \tau_{stick}} \quad (4.7)$$

To simplify the analysis the values of the pre-exponentials for hopping, sticking and thermally desorbing are taken as being equal.

Let f be the mean fraction of As_4 molecules bonded to an arsenic site, which is one of a local group, which desorb without

first leaving the group. Taking a statistical equilibrium upon the surface

$$f = \frac{e^{-E_0/k_B T}}{e^{-E_0/k_B T} + \Theta_{Ga} e^{-(E_{BB}-E_0)/k_B T}} \quad (4.8)$$

where $\Theta_{Ga} = 1 - \Theta_{As}$ and E_B and E_{BB} are the binding energies of the As_4 molecule to arsenic and gallium sites respectively. The fraction of As_4 molecules which migrate to an arsenic site from a gallium site in a small time τ_{hop} is then

$$\frac{\tau_{hop}}{\tau_{migrate}} = \frac{\Theta_{As} e^{-(E_{BB}-E_0)/k_B T}}{\Theta_{As} e^{-(E_{BB}-E_0)/k_B T} + \Theta_{Ga} e^{-E_H/k_B T}} \quad (4.9)$$

where E_H is the energy required to hop to adjacent gallium sites.

Using the equality of the pre-exponential factors for τ_{hop} and

τ_{stick}

$$\tau_{migrate} = \frac{\tau_{stick}}{\Theta_{As}} \left[\Theta_{As} e^{(E_H-E_s)/k_B T} + \Theta_{Ga} e^{(E_{BB}-E_s-E_s)/k_B T} \right] \quad (4.10)$$

where E_s is an activation energy associated with τ_{stick} .

If an arsenic molecule lands upon part of a surface which is gallium-covered, then the probability of it surviving migration to an arsenic site is given by P ; hence a fraction $(1 - p)$ will grow GaAs and contribute to S . Of the number which actually survive migration, a certain fraction $(1 - f)$ will hop back to the gallium region and the process will be repeated. The infinite series may be summed to give the fraction of the original beam which initially land upon a gallium site and stick,

$$S^{(Ga)} = \Theta_{Ga} \left\{ \frac{1-p}{1-(1-f)p} \right\} \quad (4.11)$$

In a similar fashion, the fraction sticking which initially land on an arsenic site is

$$S^{(As)} = \Theta_{As} \left\{ \frac{(1-f)(1-p)}{1-(1-f)p} \right\} \quad (4.12)$$

Combining equation (4.5) with these two terms gives

$$S = \frac{(1-p)(1-f\Theta_{As})}{1-(1-f)p} = \frac{1}{4} \Theta_{As} q \quad (4.13)$$

where $q = J_{Ga} / J_{As}$.

To evaluate the reaction order for various surface coverages, a three beam technique is used which employs the small signal approximation. The experimental technique and the results obtained by Foxon and Joyce are presented in appendix III. There, a detailed mathematical analysis is also presented, however by examining the behaviour of the equations previously derived, as the surface changes from being arsenic-rich to gallium-stabilized, the reaction orders of the As_4 adsorption-desorption process may be obtained.

When q is small, the surface is arsenic rich and the sticking coefficient is effectively zero; consequently the desorbing flux of molecules $J_{As}^{(0)}$ is approximately equal to the impinging flux:

$$J_{As}^{(0)} = (1 - S) J_{As} \quad (4.14)$$

which implies that the interaction is first order.

When q is large, however, Θ_{As} is very small and hence from equation (4.13)

$$S = \frac{1 - p}{1 - (1-f)p} \quad (4.15)$$

$$S = 1 - \frac{p f}{1 - (1-f)p} \quad (4.16)$$

As there are very few arsenic sites upon the surface, the probability, p , of an As_4 molecule migrating to one is very small. From equations (4.14), (4.15) and (4.7) neglecting second order terms

$$J_{As}^{(0)} = J_{As} f \left\{ \frac{\tau_{stick}}{\tau_{migrate}} \right\} \quad (4.17)$$

For large q ; $\Theta_{Ga} \approx 1$, $\Theta_{As} \approx 0$ and $S \approx 1$: thus from equation (4.9)

$$\tau_{migrate} = \tau_{hop} \frac{e^{-E_H/k_B T}}{\Theta_{As} e^{-(E_{GS}-E_0)/k_B T}} \quad (4.18)$$

$$\tau_{migrate} = \frac{\tau_{Transfer}}{\Theta_{As}} \quad (4.19)$$

where

$$\tau_{Transfer} = \tau_0 e^{[E_{GS}-E_0]/k_B T} \quad (4.20)$$

and is the mean time required to hop from a gallium site to an arsenic site. Substituting from equation (4.13) for Θ_{As}

$$\tau_{migrate} = \frac{\tau_{Transfer}}{4S \frac{J_{As}}{J_{Ga}}} \quad (4.21)$$

Consequently

$$J_{As}^{(0)} = \frac{4f \tau_{stick}}{J_{Ga} \tau_{Transfer}} [J_{As}]^2 \quad (4.22)$$

which implies that for a gallium rich surface the interaction is second order.

Let $\tau^{(As)}$ be the delay time for a totally arsenic covered surface, that is

$$\tau^{(As)} = \tau_0 e^{E_0/k_B T} \quad (4.23)$$

For the gallium covered surface, the measured delay time $\tau^{(Ga)}$, is therefore the sum of two components

$$\tau^{(Ga)} = \tau_{migration} + \tau^{(As)} \quad (4.24)$$

and if $E_{BB} < 2E_B$ then the rate limiting step is surface migration and

$$\tau^{(Ga)} \approx \tau_{migration} \quad (4.25)$$

As the sticking coefficient, S , has no temperature dependence in the growth regime, the slope of the Arrhenius plot (figure (IV.2)) for the gallium-covered surface will (from equations (4.25) and (4.19)) give an approximate value of $E_{BB} - E_B \approx 0.36$ eV. Alternatively, at high arsenic coverages, the slope gives $E_B = 0.53$ eV.

e) Comparison with Experiment and Discussion

To facilitate comparison with the experimentally measured data, four activation energies need to be specified. For a particular value of q chosen by experimental conditions, values are assigned to these energies and equation (4.13) is solved for S and Θ_{As} . Consequently the theoretical functional dependence of S upon q may be found and this is shown in figure (IV.3). Sets of values of the energies giving this fit are shown in table (IV.1). Values satisfying these experimental results yield

TABLE IV.1

E_H (eV)	E_S (eV)	E_B (eV)	E_{BB} (eV)
.624	.792	.526	.886
.749	.917	.526	.886
.499	.805	.526	.749
.624	.931	.526	.749
.360	.792	.526	.624

Values for the activation energies of As_4 molecules for hopping, E_H ; sticking, E_S ; and bonding to As, E_B ; and Ga, E_{BB} , sites.

Each set is capable of producing the fit to the experimental data shown in figures VI.2 and IV.3.

$$E_{BB} - 2E + E - E_H \approx 0$$

$$E_H + E_B - E_{BB} > 5 k_B T$$

and these conditions automatically ensure that the sticking coefficient is insensitive to substrate temperature in the range 450 - 600 K.

Consequently the agreement between this three-parameter model and experiment is rather encouraging. The variation of the As_4 sticking coefficient with both temperature and incident beam fluxes is quantitatively understood, and a qualitative discussion of the change in reaction order is presented. Using this model a second order reaction mechanism is obtained without assuming a direct interaction between ad molecules. This is the crucial difference between the model presented here and that of Foxon and Joyce and at present a series of experiments is being undertaken in an attempt to resolve this point.

Chapter V

ENERGY EXCHANGE PROCESSES AT A SURFACE

a) Introduction

In Chapter 1 a discussion was presented which outlined the various possible atom-surface scattering processes. Broadly speaking the events may be classed as either elastic, where no energy transfer occurs between the incident atom and surface, or inelastic when energy is transferred. When the incident beam is molecular, as opposed to atomic in nature, it is possible that energy may be transferred either to or from the molecule via additional internal modes which are unavailable to atoms.

For a molecule with S constituent nuclei, for example, there are $3S$ degrees of freedom, each of which can account for a certain fraction of the total energy of that molecule. Three of these states correspond to translational motion which are available to both atomic and molecular species. For a non-linear molecule, a further 3 states correspond to rotational degrees of freedom, the final $3S-6$ states being vibrational modes of the system (67).

The transfer of energy from a surface into internal molecular states has been experimentally observed in the desorption of H_2 from metal surfaces (68). For such a system the angular distribution of the desorbed flux does not follow the cosine law and the effective beam temperature of the H_2 was found to be consistent with a temperature in excess of the surface temperature! If one considers the accommodation of the gas molecules as being complete, then neither of these observations can be understood on classical thermodynamic grounds.

Recently work has been published (69) which suggests a similar energy exchange process for As_2 and As_4 molecules desorbing from a GaAs (111) surface. In this study a molecular beam was directed at a clean GaAs (111) surface and after scattering, the effective beam temperature was measured by a time of flight (TOF) technique. A preliminary study with a monatomic beam of gallium atoms served to calibrate the system, as the effective beam temperature of the scattered atoms should be the same as that of the surface. For both As_2 and As_4 molecular species, however, the scattered beams had velocity distributions consistent with temperatures considerably lower than that of the surface! The conclusions drawn were that the desorbing molecules were excited internally, otherwise the GaAs crystal would have gained energy when in contact with arsenic vapour in an isothermal system.

A similar study was performed by Foxon and Joyce (64) who examined the accommodation of As_4 molecules upon a GaAs (100) surface as part of the kinetic study presented in Chapter IV. Their results showed that within experimental accuracy, incident As_4 molecules were completely thermally accommodated on the GaAs substrate.

The experimental study presented here of the TOF technique attempts to resolve these contradictory results.

b) Time of flight technique

The actual system used for the series of experiments presented in this chapter is schematically shown in Figure (V.1). A beam of particles from the effusion cell is incident upon the specimen and when steady state conditions are obtained the specimen

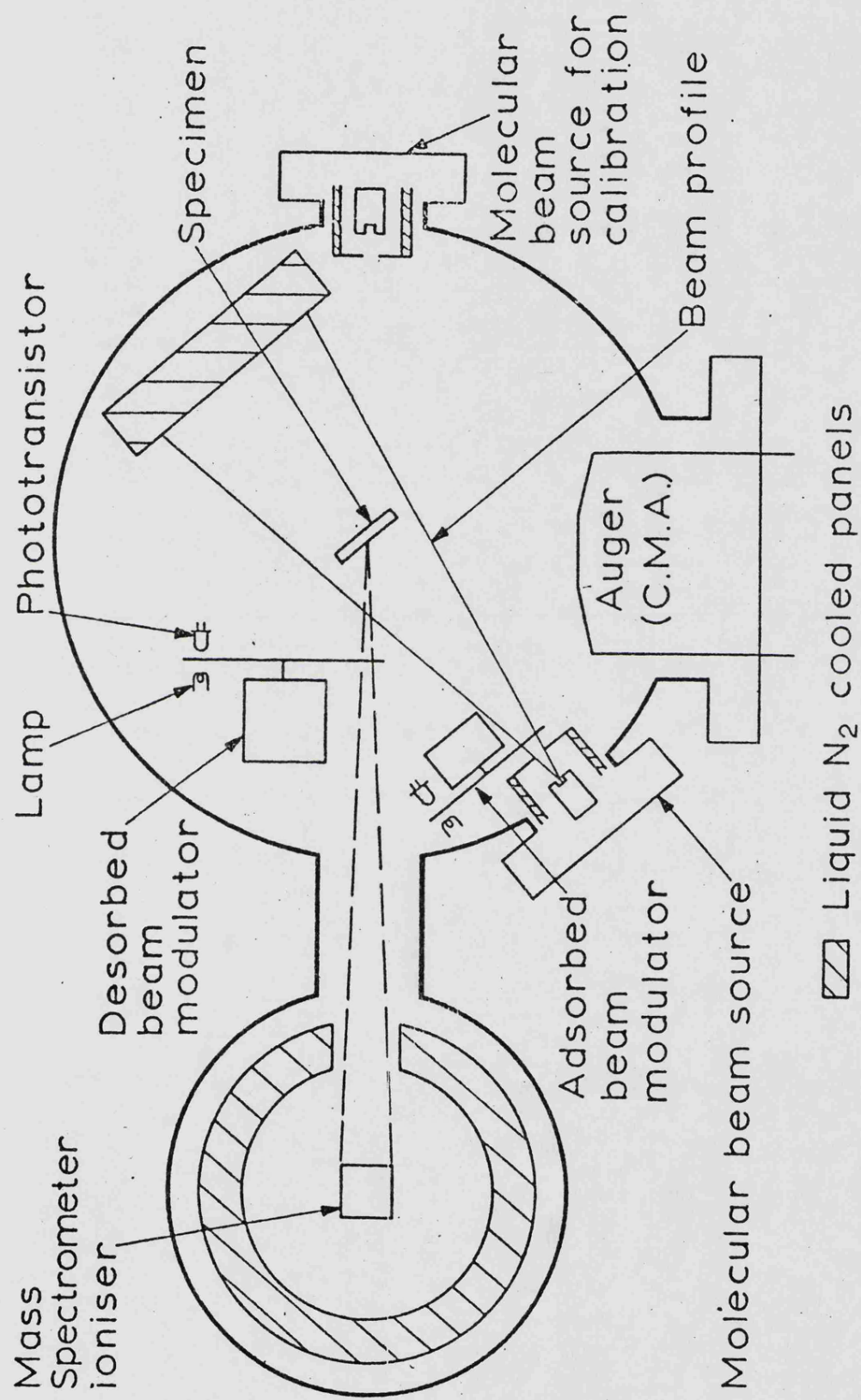


Figure V.1 General system arrangement for modulated beam experiments.

may be regarded as simply a second source of molecules. This second beam is then pulsed by interrupting it with a rotating disc into which a slit has been cut. The period between successive pulses is divided into a large number of short time intervals so that all molecules travelling from the chopper disc to the detector (in this case a mass spectrometer) are counted as single particles in the time channel corresponding to their arrival time. A time zero for each period is established by means of a synchronisation pulse derived from the chopper disc by a lamp and phototransistor, the sequence being repeated until an adequate count has accumulated in each channel.

The work presented here is concerned basically with the performance of the detector which is commonly used in such experiments, a quadrupole resonance mass spectrometer (EAI Quad 1100) with a cross-beam ionizer. The instrument is schematically shown in figure (V.2). The neutral atoms enter a small Faraday cage and some fraction are ionized by electron impact. The ions are then extracted from this cage by the application of an electric field to a focus electrode which deflects them at right angles to their original trajectory, through a small aperture. The ions then drift down the region containing four conducting rods and are subjected to oscillating electric fields which mass analyse the ion beam. The final stage of the detector is an electron multiplier which is used in an ion counting mode. A complete description of the experimental system is given in Appendix IV.

With a detector of this type, it is possible to alter various operating parameters:

- 1) The magnitude of the electric field used for extracting the ions, V_I .

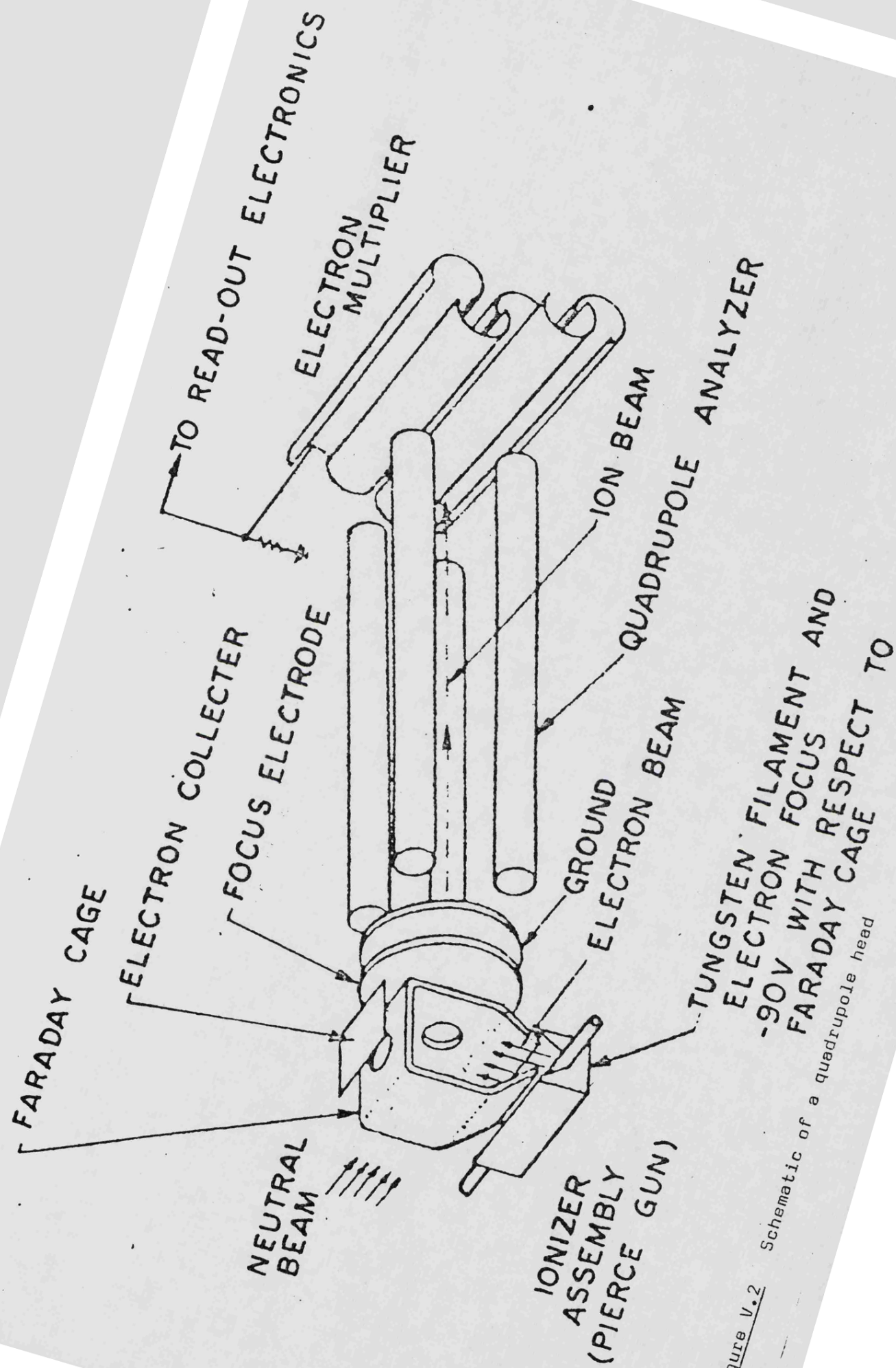


Figure V.2 Schematic of a quadrupole head
 TUNGSTEN FILAMENT AND
 ELECTRON FOCUS
 -90V WITH RESPECT TO
 FARADAY CAGE

- 2) The electron current of the ionizing beam, I_e .
- 3) The geometry of the entrance aperture for the neutral beam into the ionizer.

A series of experiments was performed which examined the behaviour of the detector as a function of these instrument parameters.

In order to calibrate the instrument, no specimen was included in the system for this set of experiments. A molecular beam from a second source was used (see Figure V.1) for this purpose, the cell being situated directly opposite the detector. For such an arrangement no exchange of energy is possible and consequently the velocity distribution within the beam will be representative of the temperature of the effusion cell, this quantity being directly measurable.

c) Theory of T.O.F. spectra

In a Knudsen cell elemental material is heated until evaporation occurs and steady state conditions between the vapour and solid are obtained (63). When this is achieved the gas has a normal Maxwell-Boltzmann velocity distribution characteristic of the temperature of the cell. A small hole in the side of the cell allows a beam of molecules to escape from the system. The diameter of this hole is less than the mean free path of the gas molecules and consequently will act as only a minor perturbation to the equilibrium system. The distribution of velocities from such a source is not of the normal Maxwell-Boltzmann form as only the faster moving molecules escape. Consequently the distribution is weighted in favour of the faster molecules; the fraction of molecules passing the modulator at a time $t = 0$ with velocity between v and $v + dv$ is

$$\left. \frac{dN}{N} \right|_v = \Phi(v) dv = 2\beta^4 v^3 e^{-\beta^2 v^2} dv \quad (5.1)$$

where

$$\beta = \frac{m}{2kT} \quad (5.2)$$

in which m is the mass of the molecules and T is the absolute temperature of the source.

This can be transformed into a TOF distribution to give the number of molecules passing a point distance L from the modulator in the time interval t to $t + dt$. If the distribution in the time domain is $f(t)$ then clearly

$$f(t) dt = \Phi(v) dv \quad (5.3)$$

since

$$v = \frac{L}{t}$$

$$f(t) = \Phi(v) \frac{dv}{dt} \quad (5.4)$$

$$f(t) = - \frac{L}{t^2} \Phi\left(\frac{L}{t}\right) \quad (5.5)$$

where the minus sign indicates that shorter times correspond to higher velocities.

Thus from (5.1) and (5.5)

$$\left. \frac{dN}{N} \right|_t = f(t) dt = 2\beta^4 \frac{L^4}{t^5} e^{-\beta^2 L^2/t^2} dt \quad (5.6)$$

If all of the molecules pass through an ionizer at the distance L , then the time-dependent number density, $\rho(t)$, in the ionizer is

obtained by dividing $f(t)$ by the velocity (L/t). In doing so

$$f(t) dt = \frac{4}{\sqrt{\pi}} \beta \frac{L^3}{t^4} \exp\left[-\beta \frac{L^2}{t^2}\right] dt \quad (5.7)$$

where the normalization

$$\int_0^{\infty} f(t) dt = 1 \quad (5.8)$$

has been employed. In deriving equation (5.7) the implicit assumption has been made that the ionizer will function as an ideal density detector.

d) Data Analysis

In TOF experiments there are two forms of modulation which may be used depending upon the length of time that the shutter remains in the open position. When a broad slot is cut into the beam chopper a large pulse of molecules passes across the system and the so-called shutter function (i.e. the fraction of the total number of molecules in the pulse as a function of time) must be deconvoluted from the time-dependent number density function given by equation (5.7) (69). For example, if the shutter function is given by $x(t)$ then the output $y(t)$ will be given by the normal convolution integral

$$y(t) = \int_0^{\infty} f(t') x(t-t') dt' \quad (5.9)$$

If the modulation is performed with a very narrow slot in the rotating disc then the opening time will be very short when compared to the molecular flight time. When this is the case, the shutter function may be approximated by a delta function $\delta(t - t')$;

consequently the integral in equation (5.9) may be directly evaluated, the output from the system being the number density function $\rho(t)$. For obvious reasons this is referred to as delta function modulation.

Clearly the latter method is more suited to the present problem, however, it can only be used if the unmodulated beam intensity and the detector sensitivity are reasonably high as there is a very large intensity loss at the narrow slot modulator. Unfortunately, for surface scattering experiments the lack of intensity prohibits use of the delta modulation technique. However, because of the large intensity from a Knudsen cell, this method was used throughout the present study.

After averaging over a suitable period of time, the output from the mass spectrometer $y(t)$ was the sum of two terms

$$y(t) = A + B\rho(t) \quad (5.10)$$

The first term A represents the background gas in the vacuum system and is essentially unrelated to the modulation frequency. B is effectively the area under the TOF spectrum once the background signal has been subtracted (equation 5.8). To establish an effective beam temperature a fit of the experimental data to equation (5.7) should be made. To obtain such a fit, an optimisation procedure needs to be adopted which will account for the background count rate and the area under the distribution curve, whilst also providing a value for the beam temperature. The technique adopted was a damped least squares method (70), the numerical analysis being performed upon a Honeywell 516 computer; typically for one spectrum the fitting procedure took ~ 20 seconds.

e) Experimental Results

Results are presented for two elements; Lead which is entirely monomeric in the vapour phase, and Arsenic whose vapour is

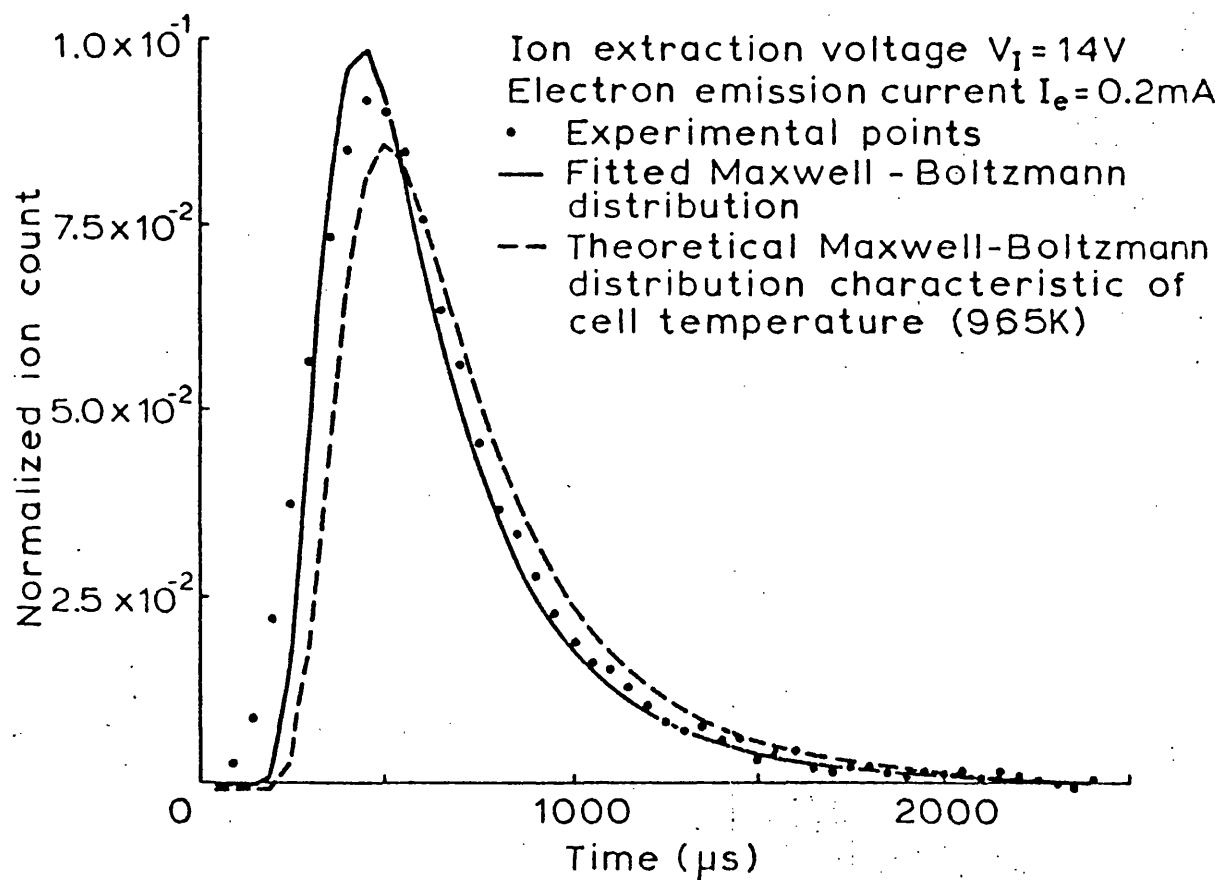


Figure V.3 Time of flight spectrum for lead.

composed of As_4 tetramers which fragment in the ioniser to give As_3^+ , As_2^+ and As^+ ions in the mass spectrometer.

For lead the expected TOF spectrum is simply the Maxwellian distribution of equation (5.7) with the effective beam temperature equal to that of the Knudsen cell. The experimental data obtained could always be fitted to such an expression however, the beam temperature obtained in this way differed significantly from that of the cell and was strongly dependent upon the operating parameters of the detector. Figure (V.3) shows a typical set of data for the TOF spectrum of a lead beam effusing from a cell at 965 K. The individual points represent the normalised ion count as a function of time, the solid line being the fitted Maxwell Boltzmann distribution. The dotted curve represents the theoretical distribution from a source at 965 K and it is clear that the measured distribution is characteristic of a cell with much higher temperature (in this particular case 1247 K!). Figure V.4 shows the ratio of the effective beam temperatures T_B , to that of the cell, T_F , as a function of the electron emission current for various values of the ion extraction voltage. A value of $T_B/T_F = 1$ is consistent with an effective beam temperature of that of the cell, and it is clearly seen that for these particular values of I_e and V_I this condition is never realised!

When elemental arsenic is used as a source material the molecular beam is composed of As_4 tetramers. This gives rise to additional effects in the ioniser to those seen for lead, as there is an appreciable cracking of the As_4 into fragmentation products after electron bombardment. Figure (V.5) shows the fitted Maxwell Boltzmann distributions (actual data points have been excluded for clarity) for the parent ion As_4^+ and for the fragment

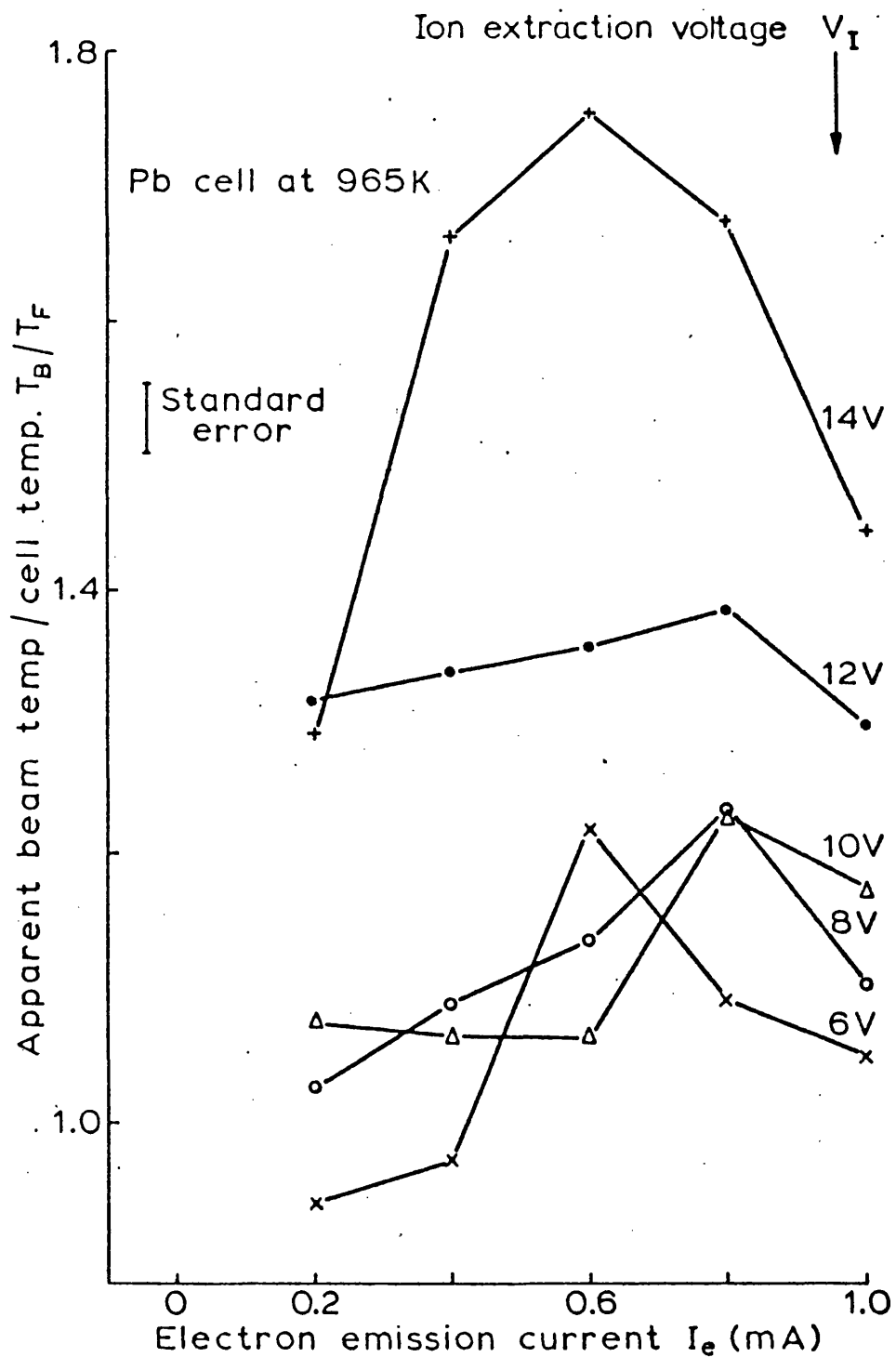


Figure V.4 : Ratio of apparent beam temperature (T_B) to cell temperature (T_F) as a function of emission current and ion-extraction voltage.

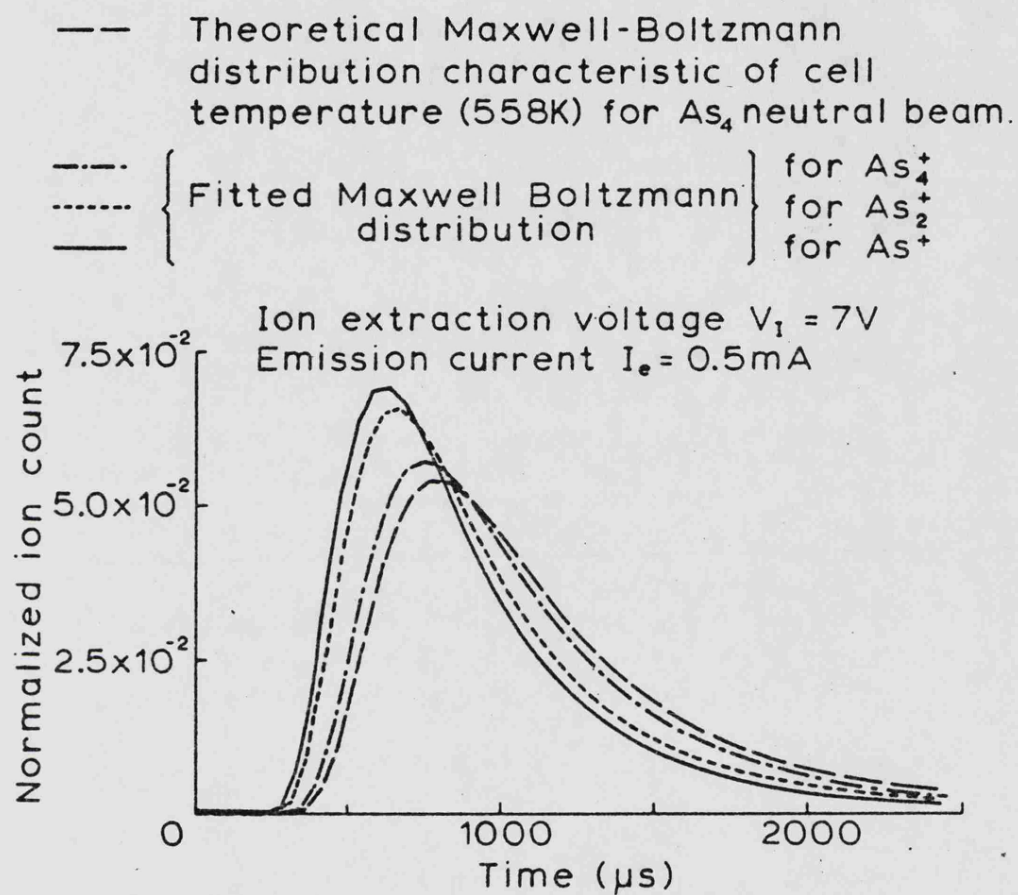


Figure V.5 : Time of flight spectra for arsenic ions from an As_4 neutral molecule beam.

ions As_2^+ and As^+ , together with a theoretical distribution corresponding to the temperature of the cell (558 K). Since there is only one parent molecule, each of these normalised distributions should be identical. As can be seen this is clearly not the case, each molecular ion having an individual distribution. The TOF spectra again were drastically affected by the operating parameters of the spectrometer and Figure (V.6) shows the beam to cell temperature ratio as a function of the ion extraction voltage for the various molecular ions.

For all of the results so far presented, the aperture of the ioniser was unrestricted. It was found that by keeping all of the operating parameters constant, the effective beam temperature could be considerably increased by confining the neutral beam to the central region of the ioniser.

f) Discussion

This is the first time that a systematic study of TOF spectra have been made as a function of the operating parameters of a quadrupole mass spectrometer. Several other authors (71,72) have noticed similar effects and these are discussed in detail in Appendix IV.

It is quite clear from the results presented that the mass spectrometer is not acting as an ideal density detector. The measured distribution is well represented by the Maxwell-Boltzmann distribution given by equation (5.7) although the experimentally determined beam temperature is not truly representative of the temperature of the cell. It is possible to define a general detector response function, $g(E, I_e, V_I)$ such that for an input function, $f(E, T_F)$, the output function is $f(E, T_B)$:

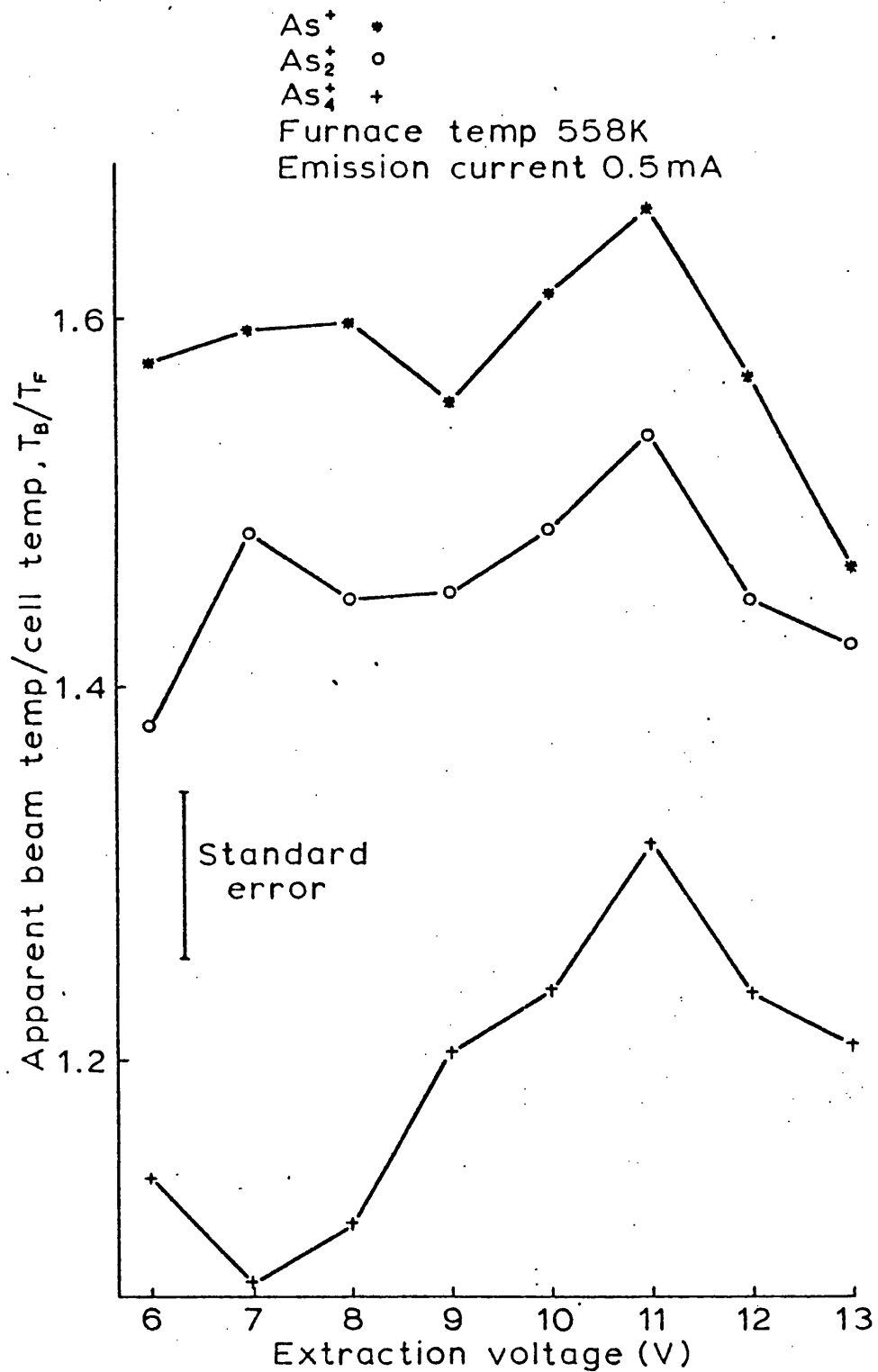


Figure V.6 Ratio of apparent beam temperature to cell temperature as a function of extraction voltage (V_1) for various fragment ions from As_4

$$f(E, T_B) = f(E, T_F) g(E, I_e, V_I) , \quad (5.11)$$

where E is the neutral molecule energy. The response function, $g(E)$, can easily be generated from the measured and theoretical spectra (e.g. Figure V.3) and is of the form

$$g(E) = \gamma \exp(\delta E) , \quad (5.12)$$

where γ and δ are inter-related functions of V_I and I_e . Figure (V.7) shows values of $g(E)$ for $T_B > T_F$, $T_B < T_F$ and also the theoretical line for the ideal case when $T_B = T_F$.

Of the two processes occurring in the ioniser, it seems most likely that it is the ion extraction process which is being affected by adjusting the quadrupole operating parameters since the actual ion formation process is less likely to be energy dependent. Changing the extraction voltage and emission current radically alters the already complex electromagnetic field within the ioniser. Although a detailed theoretical study of the field distribution is quite feasible, it would perhaps be more beneficial to design a new ionisation chamber. In its present form the quadrupole mass spectrometer was designed to be a residual gas analyser and consequently any time delays involved in the ion extraction mechanism was never of any importance. $g(E)$ is thought not to be a global function but will depend critically upon the instrument used and the degree of sophistication involved in the various ionisation and extraction processes.

Consequently any attempts to use such a system to measure the velocity distribution of a beam of neutral particles traversing the ioniser could be in serious error. It is perhaps possible in theory to calibrate the instrument for a beam of known temperature, as presented here, before studying any surface reaction products.

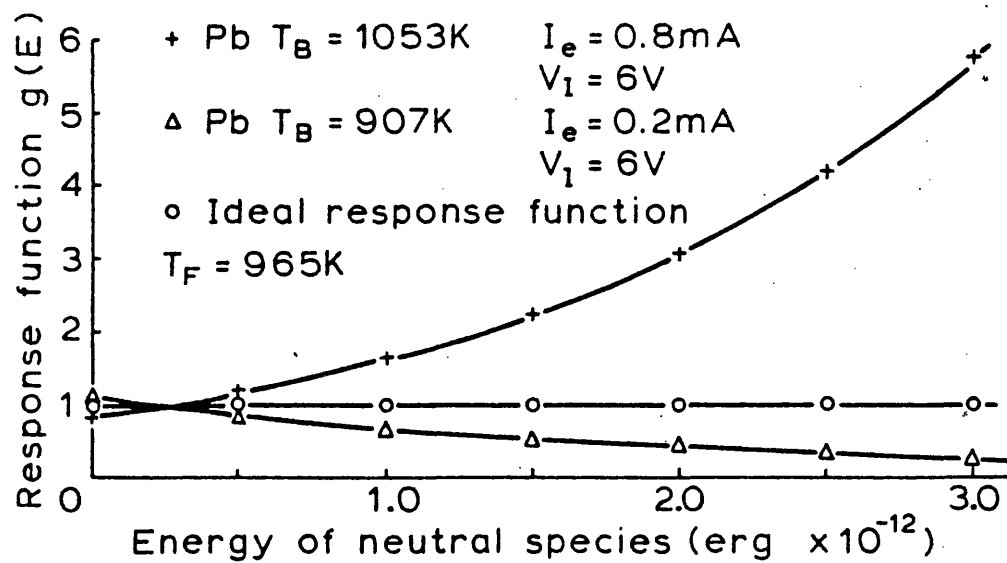


Figure V.7 Mass spectrometer response functions

However, because of the extreme difficulty in ensuring that both the known and unknown beams pass through the ioniser in the same way, it is believed that such calibration is not possible in practice.

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APPENDIX I

The theory of atomic desorption within the harmonic approximation

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Abstract. A formal extension of earlier one-dimensional theories is given for models in which the gas-surface interaction potential can be taken to be of the cut-off harmonic form. The rate equation for finite-temperature surfaces is given in one and three dimensions for the case where the adsorbed atom interacts with a single active site. It is shown that for any harmonic substrate, the three-dimensional rate equation is a function only of the physical parameters of the adatom-active site pair. The pre-exponential factor derived in three dimensions is a function of both the temperature of the surface and the desorption energy. The angular intensity distribution of the desorbed flux is shown to be predominantly cosine-like for this model. Reasonable values are obtained for the potential parameters obtained by fitting the rate equation to experimental data for the Ga-GaAs system.

1. Introduction

Since Langmuir (1916) began his original studies on the evaporation of a tungsten filament, there has been only a limited progression towards understanding desorption phenomena. Within a few years of Langmuir's work, the formalism of a rate equation by Frenkel (1924) enabled the two quantities most closely associated with this topic, the pre-exponential factor, τ_0 , and the desorption energy, E_d , to be measured experimentally. The theory behind this rate equation had its origins in the thermodynamics of gas-solid interactions and similar equations were, at about the same time, being formulated to explain thermionic emission (Richardson 1914, Dushman 1923).

Microscopically, the first attempt to explain desorption was made by Lennard-Jones and co-workers (Lennard-Jones and Devonshire 1936a, b, Strachan 1935), who studied the interaction of gases with surfaces by using a one-phonon quantum mechanical description. Although much of this work has subsequently been criticized by Bonch-Bruевич (1950), paper XI in the series (Lennard-Jones 1937) which was the only classical paper, was perhaps the first attempt to study the microscopic behaviour of surface kinetics.

With the advent of better experimental data, work on this subject was revived independently by Cabrera (1959) and Zwanzig (1959), who both demonstrated that large amounts of energy involving many phonons could be transferred from a gas to a solid. They did this by modelling the collision as one particle incident upon a stationary semi-infinite one-dimensional chain. This model has proved very useful and has been

used many times subsequently within this field. In order to improve the model, Zwanzig suggested that one might employ similar techniques to those used by Slater (1948) in his theory of unimolecular reaction rates to give the surface a temperature distribution. This in fact was done by Goodman (1966) who formulated a one-dimensional classical desorption theory along lines similar to those suggested by Zwanzig. In his paper Goodman described in some detail the effects of both bulk and surface modes of vibration (Wallis 1957) and how the desorption rate may be calculated using an identical treatment to that of Slater. The result suggests that the entire surface may be modelled by a single active centre which is coupled to the adatom by an harmonic potential. This conclusion was reached in a different form by Beeby and Dobrzynski (1971) (hereafter referred to as I) as part of a study of energy exchange in scattering phenomena. The same model was also investigated by Armand (1968) who formulated the complete time dependence of an atom colliding with a surface which is already at a fixed non-zero temperature.

Various three-dimensional calculations have been performed (Goodman 1965) but in the majority of cases it is the accommodation coefficient that is investigated and not the rate of desorption. One notable exception is the paper of Bendow and Ying (1973) who undertook a full quantum mechanical calculation and produced an exact expression for the rate of desorption. As is sometimes the case with quantum calculations, however, there seems to be a gain in the quantitative results at the expense of a qualitative understanding.

In this paper we extend the calculation of I to arrive at a form analogous to that derived by Slater (1948). This is given in §2 which also serves to develop the notation used in the later sections. By using similar techniques to those used in one dimension, the three-dimensional rate equation is then obtained in §3. In §4 we discuss the intensity as a function of angle of the desorbing flux. The gas-solid potential is taken as being harmonic with the equilibrium position centred about the active centre nearest to the desorbing atom. This scheme allows us to decouple our equations of motion and solve the problem exactly. Classical mechanics is used throughout.

2. One-dimensional desorption

In this section we aim to generalize the one-dimensional calculations of I and Beeby and Thomas (1974). Let us consider a perfectly general substrate of N different atoms harmonically coupled. We place no restriction on the number of neighbours coupled except that the desorbing atom is coupled only to the last atom in the chain. The gas-solid interaction is taken as in I to be a cut-off harmonic with the equilibrium position of the adatom at some distance from the surface. We may then write our equations of motion in the matrix form

$$\mathbf{M}\ddot{\lambda} = -\mathbf{K}\lambda \quad (1)$$

Here $\mathbf{M}$ is a diagonal matrix the first element of which is the mass, M , of the incident atom and the remaining elements the masses, m_i , of the bulk atoms, $\mathbf{K}$, the force constant matrix, is of the form

$$\mathbf{K} = \begin{bmatrix} K_{12} & -K_{12} & 0 & . & . & . & 0 \\ -K_{12} & [K_{12} + \sum_{i=3} K_{2i}] & -K_{23} & & & & \\ 0 & -K_{23} & [K_{23} + \sum K_{3i}] & & & & \\ 0 & -K_{24} & -K_{34} & & & & \\ . & & & & & & \\ . & & & & & & \\ . & & & & & & \\ 0 & & & & & & \end{bmatrix}$$

and λ is a vector consisting of the displacements of the atoms. This equation is not in the standard eigenvalue form so it is useful to define as a new basis set the eigenvectors satisfying

$$\{1\omega_\alpha^2 - \mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{-1/2}\}\chi^\alpha = 0 \quad (2)$$

where the mode labelled, α , has frequency ω_α and the set of vectors χ^α are taken to be orthonormal.

The general displacement, λ_i , and velocity, $\dot{\lambda}_i$, of the i th atom may be expressed as a summation of the modal displacements χ^α over the normal modes, α , of the system by including the appropriate time dependence

$$\lambda_i = \sum_\alpha A^\alpha \chi_i^\alpha m_i^{-1/2} \cos(\omega_\alpha t - \phi_\alpha) \quad (3a)$$

$$\dot{\lambda}_i = -\sum_\alpha A^\alpha \omega_\alpha \chi_i^\alpha m_i^{-1/2} \sin(\omega_\alpha t - \phi_\alpha). \quad (3b)$$

The amplitudes A^α and phases ϕ_α are at this stage undetermined. The energy of this system is given by

$$E = \frac{1}{2}[\dot{\lambda}^\dagger \mathbf{M} \dot{\lambda} + \lambda^\dagger \mathbf{K} \lambda]$$

so that substituting for λ and $\dot{\lambda}$ we obtain

$$E = \frac{1}{2} \sum_\alpha (A^\alpha \omega_\alpha)^2. \quad (4)$$

Using this energy expression in the Maxwell-Boltzmann distribution

$$P(E) = \exp(-E/kT) \quad (5)$$

the normalized distribution for a particular mode is

$$P(A^\alpha) dA^{\alpha^2} = \frac{\omega_\alpha^2}{2kT} \exp\left(-\frac{(A^\alpha \omega_\alpha)^2}{2kT}\right) dA^{\alpha^2} \quad (6)$$

where T is the temperature of the system. This is the general form of equation (8) in I.

The criterion selected for desorption to occur requires the relative separation of the adatom, with respect to some active centre, to exceed some critical value, R_c , after which the adatom is in field-free space. The relative displacement and velocity are

$$r = \lambda_a - \lambda_0 = \sum_\alpha A^\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \cos(\omega_\alpha t - \phi_\alpha) \quad (7a)$$

$$\dot{r} = \dot{\lambda}_a - \dot{\lambda}_0 = -\sum_\alpha A^\alpha \omega_\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \sin(\omega_\alpha t - \phi_\alpha) \quad (7b)$$

where the suffixes *a* and 0 refer to the adatom and active centre respectively. (Note that, unlike I, we have allowed the adatom to be of a different mass from the atoms in the surface.) Following the treatment in I we now calculate the probability of the adatom having position *R* and velocity $\dot{R}$ with respect to the active centre. This is given by

$$P(R, \dot{R}) = \langle \delta(R - r) \delta(\dot{R} - \dot{r}) \rangle \quad (8)$$

$$= \langle \delta \left\{ R - \sum A^\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \cos(\omega_\alpha t - \phi_\alpha) \right\} \\ \times \delta \left\{ \dot{R} + \sum A^\alpha \omega_\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \sin(\omega_\alpha t - \phi_\alpha) \right\} \rangle \quad (9)$$

the average being taken over the equilibrium distribution for the surface at temperature *T*. The amplitudes are given by the probability distribution (6) and the phases are random. The leading non-zero terms in this average are

$$\langle [\sum A^\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \cos \phi_\alpha]^2 \rangle = kT \sum_\alpha \frac{1}{\omega_\alpha^2} (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \\ = kT/K_{12} \quad (10)$$

and

$$\langle [\sum A^\alpha \omega_\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \sin \phi_\alpha]^2 \rangle \\ = kT \sum_\alpha (\chi_a^\alpha M^{-1/2} - \chi_0^\alpha m_0^{-1/2}) \\ = kT(M + m_0)/Mm_0 = kT/W \quad (11)$$

where *W* is a reduced mass. The complete series may be summed exactly to give

$$P(R, \dot{R}) = [(K_{12}W)^{1/2}/(2\pi kT)] \exp [-(R^2 K_{12} + \dot{R}^2 W)/2kT] \quad (12)$$

as the final probability.

From I the rate of desorption is given by

$$\tau^{-1} = \int_0^\infty d\dot{R} \dot{R} P(R, \dot{R}) \quad (13)$$

which substituting from (12) gives

$$\tau^{-1} = [(K_{12}W)^{1/2}/2\pi] \exp(-R_c^2 K_{12}/2kT). \quad (14)$$

The calculation of Beeby is thus finally reduced to the expression found by Slater (1948), the pre-exponential is a function simply of the physical variables of the active centre-adatom pair. Again the desorption energy is the work required to escape from the bottom of the harmonic potential.

3. Three-dimensional desorption

The three-dimensional model substrate will be taken to be a perfectly general lattice in the harmonic approximation. In order to demonstrate the procedure for calculation, consider the case of a monatomic substrate with central forces only; the more general case is given in the Appendix. As only central forces act, we may decouple our system and so reduce the problem to one of three mutually perpendicular chains, each containing the active centre as a constituent atom, as shown in figure 1. The normal modes

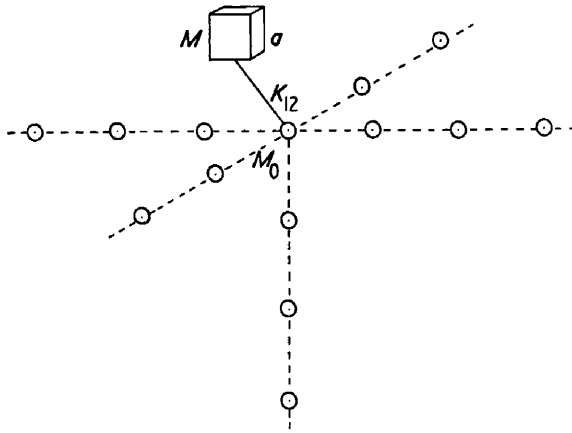


Figure 1. Illustration of the three perpendicular chains used in the three-dimensional desorption calculation. The broken lines correspond to harmonic coupling.

of the decoupled systems may be calculated as before and summations over the normal modes of the eigenvectors may be performed¹. The displacement of the adatom with respect to the active centre is given by

$$r_{\epsilon} = \lambda_{a,\epsilon} - \lambda_{0,\epsilon} = \sum_{\alpha} A_{\epsilon}^{\alpha} (\chi_{a,\epsilon}^{\alpha} M^{-1/2} - \chi_{0,\epsilon}^{\alpha} m_0^{-1/2}) \cos(\omega_{\alpha,\epsilon} t - \phi_{\alpha,\epsilon}) \quad (15a)$$

$$\dot{r}_{\epsilon} = \dot{\lambda}_{a,\epsilon} - \dot{\lambda}_{0,\epsilon} = - \sum_{\alpha} A_{\epsilon}^{\alpha} \omega_{\alpha,\epsilon} (\chi_{a,\epsilon}^{\alpha} M^{-1/2} - \chi_{0,\epsilon}^{\alpha} m_0^{-1/2}) \sin(\omega_{\alpha,\epsilon} t - \phi_{\alpha,\epsilon}) \quad (15b)$$

where the subscript ϵ runs over the directions x, y, z . Again we shall calculate the probability of the displacement being equal to the particular values R and $\dot{R}$

$$\begin{aligned} P(R, \dot{R}) &= \langle \delta(R - r) \delta(\dot{R} - \dot{r}) \rangle \\ &= \int dr d\dot{r} P(r_x, \dot{r}_x) P(r_y, \dot{r}_y) P(r_z, \dot{r}_z) \delta(\dot{R} - \dot{r}) \delta(R - r) \end{aligned} \quad (16)$$

where

$$r = (r_x, r_y, r_z) \quad \text{and} \quad \dot{r} = (\dot{r}_x, \dot{r}_y, \dot{r}_z).$$

Following the one-dimensional calculation we may immediately write

$$P(r_x, \dot{r}_x) = (K_{12} W)^{1/2} / (2\pi kT) \exp[-(r_x^2 K_{12} + \dot{r}_x^2 W) / 2\pi kT] \quad (17)$$

with similar expressions existing for $P(r_y, \dot{r}_y)$ and $P(r_z, \dot{r}_z)$. Thus on substitution into (16) the probability is

$$P(R, \dot{R}) = \Phi \int dr d\dot{r} \exp(-vr^2) \exp(-\mu \dot{r}^2) \delta(R - r) \delta(\dot{R} - \dot{r}) \quad (18)$$

where we have defined

$$\begin{aligned} \Phi &= (K_{12} W)^{1/2} / 2\pi kT \\ v &= K_{12} / 2kT \quad \text{and} \quad \mu = W / 2kT. \end{aligned} \quad (19)$$

So far, this calculation has followed the one discussed in § 2; however in using (18) we must apply restrictions appropriate to three dimensions in order to calculate the desorption rate. This is given by

$$\tau^{-1} = \int d\dot{R} R_c^2 \sin \xi \, d\xi \, d\psi \, \dot{R}_{\perp} P(R_c, \dot{R}) \Theta(R \cdot \dot{R}) \Theta(\xi_c - \xi) \quad (20)$$

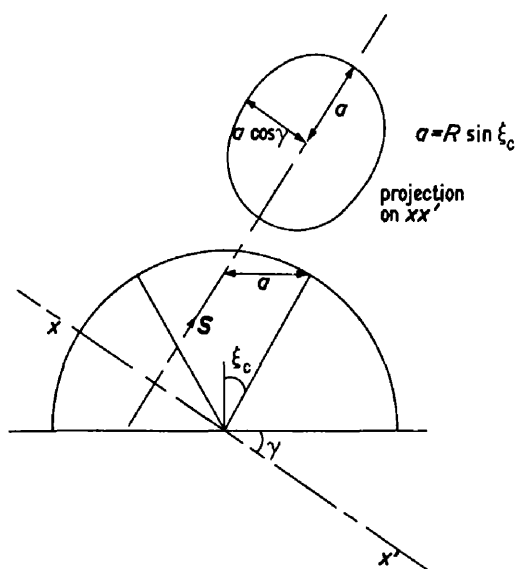


Figure 3. Illustration of the technique used to evaluate the angular intensity distribution. The area of the cap projected on to the plane xx' is proportional to the intensity in the direction S .

illustration, a spherical cap will be used for which $\xi \leq \xi_c$.† From figure 3 it can be seen that the element of area $\sin \xi d\xi d\psi \cos \delta$ is the projection of the relevant surface area of the cap upon the plane whose normal is given by S . The final expression for the angular intensity is then

$$\begin{aligned}
 I(S) &\propto \pi \sin^2 \xi_c \cos \gamma + \Theta[(\xi_c + \gamma) - \tfrac{1}{2}\pi] (B - \pi \sin^2 \xi_c \cos \gamma) \\
 B &= \sin^2 \xi_c \cos \gamma [\tfrac{1}{2}\pi + \sin^{-1}(\cot \xi_c \cot \gamma) \\
 &\quad + \cot \xi_c \cot \gamma (1 - \cot^2 \xi_c \cot^2 \gamma)^{1/2}] \\
 &\quad + \cos^{-1}(\cos \xi_c \operatorname{cosec} \gamma) - \cos \xi_c \operatorname{cosec} \gamma (1 - \cos^2 \xi_c \operatorname{cosec}^2 \gamma)^{1/2} \quad (24)
 \end{aligned}$$

and γ is the angle between S and the surface normal.

This quantity is plotted for various values of the polar cap angle ξ_c in figure 4. In

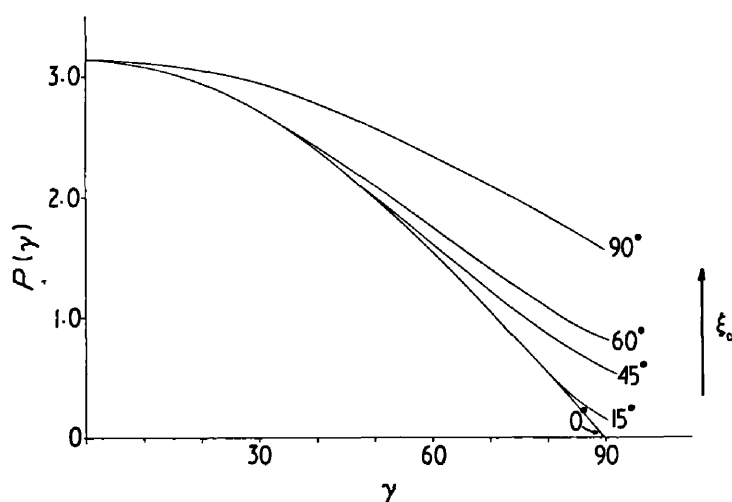


Figure 4. $P(\gamma)$ calculated for various values of ξ_c using equation (24).

† Surface unit cells do not usually deviate greatly from circles so it is thought that this is a realistic approximation.

the limit of $\xi_c \rightarrow \frac{1}{2}\pi$ the expression reduces to $\frac{1}{2}\pi(1 + \cos \gamma)$ whereas if $\xi_c \rightarrow 0$ then we approach the familiar cosine distribution. Further to the previous discussion of hopping to an adjacent site when $\gamma > \xi_c$ a certain fraction of atoms that have been counted as desorbed will in fact re-enter the sphere of influence of an adjacent atom and so will not immediately leave the surface. Thus $I(S)$ as calculated, is expected to be too large when $\gamma > \xi_c$. It is possible to calculate the correction term but this is of no value since most experimental data for this region suffers acutely from poor counting statistics.

5. Comparison of the rate formula with experimental data

Desorption data are available for many systems—gases on metals, alkalis on metals and so on. However, in order to compare our formula (22) with experiment, we select the results of Arthur (1968) who measured the delay time of atomic gallium on the compound semiconductor gallium arsenide. This material provides us with a source of valuable data due to the particular interest in its fabrication by molecular beam epitaxy. We principally concern ourselves with the delay time of Ga on the arsenic stabilized (Cho *et al* 1970) (111) polar face of GaAs.

For such a hexagonal crystal face it can be determined geometrically that the angle defining the cap is

$$\xi_c = \sin^{-1}(b/2R_c) \quad (25)$$

where b is the interatomic separation on the particular face being studied. Substituting this into (22) and using the values for GaAs given in table 1, we obtain the best agreement with experiment when $R_c = 2.61 \text{ \AA}$ and $K_{12} = 12.2 \text{ K dyne cm}^{-1}$. With these values inserted into (25) we obtain $\xi_c = 54^\circ$ which gives only a slight deviation from a cosine distribution.

Table 1. Set of values used in §5, obtained from Arthur (1968) (cgs units).

M_{Ga}	M_{As}	b	E_d	ν_0
1.16×10^{-22}	1.25×10^{-22}	4.22×10^{-8}	4.1×10^{-12}	1.6×10^{-14}

The critical distance derived in this way is in satisfactory agreement with the surface dimensions and the force constant. Somewhat smaller than that for bulk GaAs as derived from the phonon spectrum, appears entirely reasonable. Also the observed desorption follows a cosine distribution (T Foxon 1975 private communication).

6. Discussion and conclusions

By a straightforward extension to the work of Beeby and co-workers, a three-dimensional model explaining desorption phenomena has been formulated. By using a simple gas-surface potential, we are able to understand the major physical processes influencing the desorption rate. This calculation thus has significant advantages over some of the 'exact solutions' which give very little information about the surface interactions which

determine desorption. It is shown that the rate equation contains both temperature and energy dependence in the exponent and the pre-exponential, a result not predicted in one dimension. The comparison of this theory with experiment is also satisfactory. The calculated distance, R_c , at which the atom-surface interaction ceases, and the force constant K_{12} , should not be taken as definitive because of the simplicity of the interaction potential used.

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Appendix

The general three-dimensional case can be described by extending equation (2) to define the set of $3(N + 1)$ eigenvectors which describe the movement of the system of N surface atoms plus an adsorbed atom. The $3(N + 1)$ components of each vector χ^α are then triplets of cartesian model displacements for the $(N + 1)$ atoms and may be labelled $\chi_{i,\epsilon}^\alpha$ ($\epsilon = x, y, z$). The χ^α thus defined are again an orthonormal set. Equations (15) are thus still applicable except that now the x, y, z directions will not be assumed independent as in equation (16). By Fourier transform of the first line of (16)

$$P(R, \dot{R}) = \frac{1}{(2\pi)^6} \langle \exp(-i\rho \cdot r) \exp(-iq \cdot \dot{r}) d\rho dq \exp(i\rho \cdot R) \exp(iq \cdot \dot{R}) \rangle \quad (A.1)$$

Expanding the exponentials using (15), averaging as in §2 and using the orthonormality of the χ^α gives

$$\langle \exp(-i\rho \cdot r) \exp(-iq \cdot \dot{r}) \rangle = \exp(-\rho^2 kT/2k_{12}) \exp(-q^2 kT/2\omega).$$

As in §2 and §3 it has here been assumed that the adatom couples only to one site. Completing the ρ and q integrals in (A.1) reproduces equation (18).

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behaviour of the phase shift, an Arrhenius plot for the delay time can be made which approximates to Frenkel's equation

$$\tau = \tau_0 \exp(E_d/k_B T)$$

yielding a pre-exponential factor τ_0 , and a desorption energy E_d , where k_B is Boltzmann's constant.

Prior to 1937 the adsorption-desorption process was discussed in terms of bulk thermodynamic quantities. In 1937 a microscopic view of desorption was attempted by Lennard-Jones (1937), who modelled the system by a linear, harmonically-coupled chain, desorption occurring when one of the bonds exceeded a critical length. This theory has been used as a starting point by many subsequent authors and much of our present understanding stems from such work (Zwanzig 1960). Most calculations to date have been for systems where the adatom interacts with a single atom (active centre) of the substrate via a harmonic potential, as this allows a simple representation of the atomic motions by a superposition of a set of phonon modes of the system. Jewsbury and Beeby (1975, hereafter referred to as I), however, have presented a thorough classical analysis in one dimension, where the bonding of the adatom to the active site and all of the interactions within the 'solid' are represented by general potentials.

This paper begins by performing a numerical analysis of the delay-time expression derived in I using a model potential of the Morse form. Results for physisorbed and chemisorbed systems are presented in §2 and comparison with experimental results made. A formal mathematical extension of the equations derived in I to three dimensions is given in §3. Numerical results using a Morse interaction are presented in §§4 and 5, when we also discuss any angular dependence that may occur in the pair potential. Comparison with experimental data is again presented.

2. One-dimensional desorption: numerical results

The delay time represents the length of time an atom resides upon a surface. Experimentally, both the source and the detector are finite distances from the surface and consequently the time taken for an atom to cover these distances must be subtracted from the total time measured. As was shown by Jewsbury and Beeby (1975) the same procedure, i.e. the subtraction of a transit time, must be performed in a theoretical analysis to obtain the rate of desorption. In I it was shown that in one dimension the delay time, τ , is

$$\tau = \lim_{x_c \rightarrow \infty} (2\pi\mu/k_B T)^{1/2} \left[\int_{-\infty}^{x_c} dx \exp(-V(x)/k_B T) \right] - t_0(x_c) \quad (1)$$

where μ is the reduced mass of the adatom active centre pair, T is the surface temperature, $V(x)$ is the gas-solid potential, t_0 is the transit time and k_B is Boltzmann's constant. For a realistic potential $V(x)$ goes to 0 for large x and the limit is well defined. It was shown in I that when the potential is a cut-off harmonic centred about d with spring constant κ :

$$\begin{aligned} V(x+d) &= \frac{\kappa}{2}(x^2 - x_c^2) & -\infty < x < x_c \\ V(x+d) &= 0 & x > x_c. \end{aligned} \quad (2)$$

An approximate expression for the delay time is

$$\tau = \pi(\mu/\kappa)^{1/2} \{1 + \operatorname{erf}[(\kappa/2k_B T)^{1/2} x_c]\} \exp(\kappa x_c^2/2k_B T) - 2\pi(m/\kappa)^{1/2}. \quad (3)$$

Typically, the final term will have a value of the order of the time taken for a particle to complete one oscillation within the potential well ($2\pi\sqrt{(m/\kappa)} \simeq 10^{-12}$ s), which when compared with measurable delay times ($\simeq 10^{-5}$ s) may justifiably be neglected. Further, for most systems in which the delay time may be measured, the error function may be approximated to unity, whereby

$$\tau = 2\pi(\mu/\kappa)^{1/2} \exp(\kappa x_c^2/2k_B T) \quad (4)$$

an expression obtained independently by Holloway and Beeby (1975) by an equation-of-motion technique. It is interesting to note, however, that in expression (3) a temperature dependence appears outside the exponent. Under such conditions the pre-exponential and desorption energy are ill defined but can be assigned by adopting as an expression for the pre-exponential

$$\tau_0(T) = \tau \exp(-D/k_B T) \quad (5)$$

where D is the well depth.

The actual form taken for a gas-solid potential will affect the calculated delay time. As a gas atom approaches the surface from infinity it will be accelerated by long-range dispersive forces arising from a Van der Waals like coupling between the atom and the solid. As the atom gets closer to the surface it will be repelled by the localized short-range forces resulting as the atomic and solid electron orbitals overlap. These two competing forces give rise to a potential minimum above the surface where the gas atom is most likely to be found during adsorption. Ideally a self-consistent electron scheme should be adopted for the calculation of exact gas-solid potentials, however, this is beyond present capabilities and several model potentials have been proposed as approximations (Logan and Keck 1968, Jewsbury 1975). In the discussion presented here the Morse potential is used:

$$V(r) = D\{\exp[-2(r-d)a] - 2\exp[-(r-d)a]\} \quad (6)$$

where D is the depth of the attractive well, a is an inverse length parameter which is related to the halfwidth of the potential and d is the position of the potential minimum. This potential has a short-range repulsive part plus a long-range exponential attraction which dies off slowly at large distances from the surface. A two-parameter potential, similar to those used in bulk calculations (e.g. Lennard-Jones), could have been used; however, the additional flexibility obtained by using the Morse potential is desirable when dealing with the surface problem: the extra parameter allows the possibility of overlayer spacings being different from bulk near-neighbour separations.

We may approximate the transit time in such a potential by that in an harmonic one where the parameters are obtained by fitting the two potentials around their minima. Then

$$t_0(x_c) = \frac{2}{\bar{v}} \left[x_c - \left(d + \frac{1}{a} \right) \right] + 2\pi(m/2Da^2)^{1/2} \quad (7)$$

where the first term corresponds to the time taken for an atom moving with velocity $\bar{v}$ to traverse the distance from the detector at x_c where the potential is almost zero, to the

beginning of the strong attractive potential. The second term represents the time taken to turn the incident atom around in the harmonic well. The delay time is given by

$$\tau = \lim_{x_c \rightarrow \infty} (2\pi\mu/k_B T)^{1/2} \left[\int_{-\infty}^{x_c - d} dy \left\{ \exp[-V(y + d)/k_B T] - \Theta\left(y + \frac{1}{a}\right) \right\} \right] - 2\pi(m/\kappa)^{1/2} \quad (8)$$

and this is quite independent of d . Θ is the Heaviside step function.

As mentioned previously, experiments often measure both the pre-exponential and the desorption energy and therefore, as the delay time in equation (8) is specified by two variables D and a , we should be able to assign a potential uniquely to any particular system. To investigate this numerically, the delay time is evaluated for two systems, one corresponding to chemisorption, the other physisorption. As a typical chemisorbed system the data of Arthur (1968) for the interaction of atomic gallium with the $(\bar{1}\bar{1}\bar{1})$ polar face

Table 1. Values used for numerical analysis, typical of chemisorption and physisorption (CGS units) M_{adatom} = mass of adatom, $M_{\text{substrate}}$ = mass of surface atom, ρ_s = density of surface active sites, E_d = desorption energy and τ_0 the pre-exponential factor.

System	M_{adatom}	$M_{\text{substrate}}$	ρ_s	E_d	τ_0
Ga-GaAs	1.16×10^{-22}	1.20×10^{-22}	3.61×10^{14}	4.1×10^{-12}	1.6×10^{-14}
			1.80×10^{14}		
K-W	3.17×10^{-23}	1.23×10^{-22}	2.20×10^{15}	2.96×10^{-12}	2.20×10^{-12}
Ne-LiF	1.672×10^{-23}	1.504×10^{-23}	—	2.40×10^{-14}	—

of GaAs was chosen. The integral in (8) was evaluated numerically using a Simpsons-rule technique in intervals from n/a to $(n + 1)/a$ using values from table 1. The result was given by the summation from $n = -3, -2, -1 \dots$, up to a value where convergence was achieved. A fit to the experimental results gives $a = 1.239 \times 10^9 \text{ cm}^{-1}$ corresponding to a Morse potential of halfwidth $8 \times 10^{-10} \text{ cm}$, the desorption energy was 4.1×10^{-12}

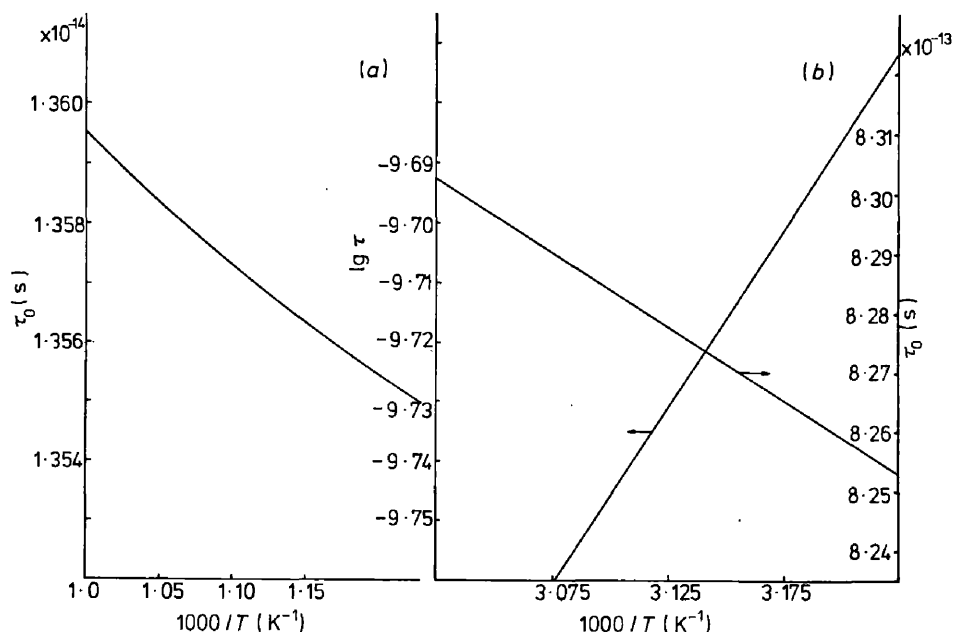


Figure 1. (a) One-dimensional calculation of $\tau_0(1/T)$ for Ga-GaAs $(\bar{1}\bar{1}\bar{1})$; (b) variation of the delay time and pre-exponential for Ne-LiF with temperature.

erg. The width of the potential well is small when compared with other gas–solid systems. The values obtained are in good agreement with those found by Holloway and Beeby (1975). Any temperature variation in the pre-exponential factor would be far too small to observe with the temperature range considered (figure 1a).

Figure 1(b) shows an Arrhenius plot and the temperature variation of the pre-exponential factor using the potential parameters typical of the Ne–LiF (001) system (table 1). This demonstrates quite clearly the order of magnitude of the delay time that one might expect from a weakly-bound system and illustrates why delay times for such systems are experimentally undetectable. Again an harmonic potential with parameters corresponding to a fit around the minimum of this Morse potential gives agreement with the delay times shown in figure 1(b). Any temperature dependence of the pre-exponential is far too small to be measured.

We can conclude that, with the exception of the slight temperature dependence of the pre-exponential factor, the simple harmonic result (4) is able to reproduce the experimental delay times almost as accurately as the result using a Morse potential.

3. Three-dimensional desorption

The techniques used in I can be simply generalized provided the adatom is assumed to interact with only one surface atom at a time. The procedure (of I) is to add to the real adatom potential, a term representing an infinite repulsive barrier placed somewhere in the region where the potential is approximately zero. The position or shape of this barrier does not affect the calculated value of the delay time (as will be seen from equation (17)).

In the three-dimensional situation there is the additional flexibility in the motion of the adatom in that it may hop between active sites before desorbing. Thus an obvious choice is for the barrier to be approximately an extension of the boundary of the surface Wigner–Seitz zones up to some fixed height. Only the striking of the top of the barrier by the adatom is to be associated with its being desorbed and reintroduced into the system. The adatom striking the side walls can be considered as equivalent to the equilibrium exchange of atoms between neighbouring surface-active sites. However, in the most natural extensions of I, within this analysis, the barrier is placed at a fixed distance r_c from the surface atom. Thus the rate of striking the barrier is

$$R = \int d\mathbf{r} \, d\mathbf{\dot{r}} \cdot \hat{\mathbf{r}} \, \Theta(r - r_c) \Theta(\xi_c - \xi) P(r_c, \mathbf{\dot{r}}) \quad (9)$$

where $P(r_c, \mathbf{\dot{r}})$ is the probability of finding an atom at position r_c with velocity $\mathbf{\dot{r}}$. The spherical polar coordinates of $\mathbf{r}$ and $\mathbf{\dot{r}}$ are

$$\begin{aligned} \mathbf{r} &= [r, \xi, \phi_r] \\ \mathbf{\dot{r}} &= [\dot{r}, \theta_r, \phi_r] \end{aligned} \quad (10)$$

We argue along the lines of Holloway and Beeby (1975) in that only particles with a positive component of momentum along the surface normal contribute to the desorbing flux and that these particles must pass through a cap of polar angle $\xi_c(r_c)$.

Within the classical regime $P(r_c, \mathbf{\dot{r}})$ is given by the Maxwell–Boltzmann distribution function. Substituting this into equation (9) the coordinates of all the surface atoms, bar one, cancel leaving a two-body expression (Kimball 1938). As in I, writing this in terms of relative and centre-of-mass coordinates gives

$$\frac{1}{R} = \frac{1}{Z} \int_{\substack{\text{All space} \\ r < r_c}} dr \int d\dot{r} \exp(-V(r)/k_B T) \exp(-\mu \dot{r}^2/2k_B T) \quad (11)$$

where

$$Z = \int_0^{\xi_c} d\xi \sin \xi \int_0^{2\pi} d\phi_r \int_0^{\pi/2} d\theta_r \sin \theta_r \cos \theta_r \int_0^{2\pi} d\phi_r \int_0^\infty dr r^2 \delta(r - r_c) \\ \times \exp(-V(r)/k_B T) \int_0^\infty d\dot{r} \dot{r}^3 \exp(-\mu \dot{r}^2/2k_B T).$$

Upon integration this becomes

$$\frac{1}{R} = (\mu/2\pi k_B T)^{1/2} \frac{\int_{\substack{\text{All space} \\ r < r_c}} dr \exp(-V(r)/k_B T)}{2r_c^2(1 - \cos \xi_c)}. \quad (12)$$

Associated with each surface-active centre is an element of area πr_{ws}^2 , where r_{ws} is the surface Wigner-Seitz radius. The density of surface active sites ρ_s therefore is

$$\rho_s = \frac{1}{\pi r_{ws}^2}. \quad (13)$$

In the limit of $r_c \rightarrow \infty$ it is clear that $\xi_c \simeq r_{ws}/r_c$, thus

$$\left. \frac{1}{2r_c^2(1 - \cos \xi_c)} \right|_{\lim_{r_c \rightarrow \infty}} = \frac{1}{r_{ws}^2}. \quad (14)$$

Using this result, the delay time is given by

$$\tau = \frac{1}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \int_{\substack{\text{All space} \\ r < r_c}} dr \exp(-V(r)/k_B T) - t_0 \quad (15)$$

where t_0 is the transit time of the adatom. As seen in one dimension, t_0 ensures convergence in r space and again we may assign an approximate value given by

$$t_0 = \frac{1}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \int_{\substack{\text{All space} \\ r < r_c}} dr \quad (16)$$

where we have simply put $V(r) = 0$ in equation (12) implying that the transit time is calculated for an atom moving in field-free space. The delay time is given by

$$\tau = \frac{1}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \int_{\text{All space}} dr [\exp(-V(r)/k_B T) - 1]. \quad (17)$$

If the potential is independent of ξ and ϕ_r , we may immediately evaluate the angular integrals giving

$$\tau = \frac{4\pi}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \int_0^\infty dr r^2 [\exp(-V(r)/k_B T) - 1]. \quad (18)$$

For computation we again take the gas-solid interaction to be a Morse potential as defined by (6). The major contribution to the resulting integral comes from the region

close to the potential minimum and hence the integral may be approximated by Laplace's method to give

$$\tau = \frac{4\pi}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \exp(-V(d)/k_B T) \int_{-\infty}^{\infty} dr r^2 \exp[-V''(d)(r-d)^2/2k_B T] \quad (19)$$

where we have effectively made a Taylor expansion of $V(r)$ to second order about the bottom of the well. For the Morse potential the approximate delay time is

$$\tau = \frac{4\pi}{r_{ws}^2} (\mu/2a^2 D)^{1/2} \left(d^2 + \frac{k_B T}{2a^2 D} \right) \exp(D/k_B T) \quad (20)$$

In order to carry out such a procedure it is necessary for the potential to satisfy the criterion that $V(0) \gg k_B T$ which places a lower limit on the value allowed for d .

4. Three-dimensional analysis with a spherically symmetric potential

The system of potassium ions desorbing from a polycrystalline tungsten surface (Isa *et al* 1972) provides useful data with which to compare the rate equation (18). The calculations are performed in the same manner as in one dimension but the results are presented in a different form since τ is now a function of all three Morse-potential parameters. We choose to present the results as plots of d against a^{-1} where each value upon such a curve satisfies the experimentally measured values of τ_0 and E_d . For the potassium-tungsten system we have taken the density of active sites as being the average atomic

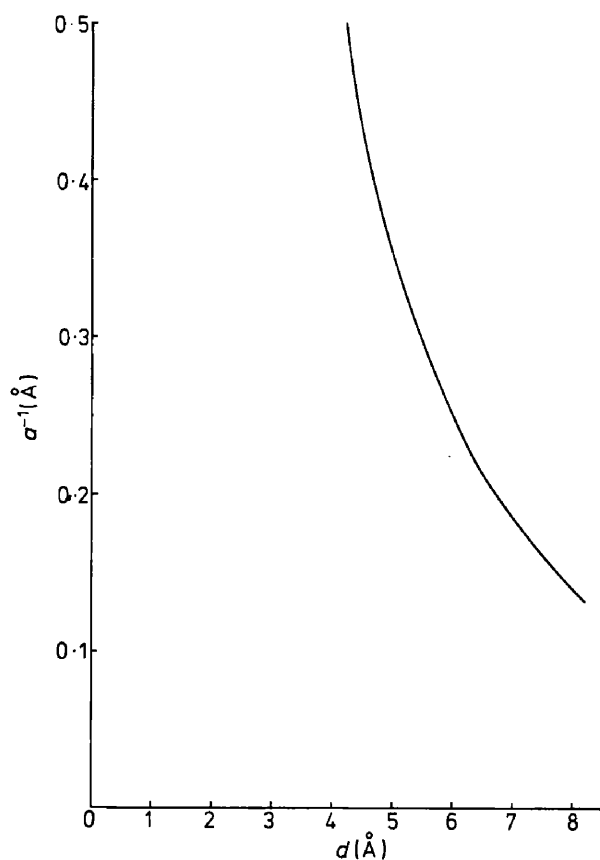


Figure 2. Variation of the potential parameters a^{-1} and d capable of reproducing experimental results for K-polycrystalline tungsten.

surface density of the low-index surface planes of tungsten (see table 1). The results of the calculations for this system are shown in figure 2 and are quite encouraging, resulting in a potential with a realistic halfwidth at about a 3 Å separation.

The Ga-GaAs ($\bar{1}\bar{1}\bar{1}$) system was also investigated using the three-dimensional equations. This is a more complicated system and the density of active sites is uncertain.

The active site in chemisorption is known to play a significant role in the physical process. Ideally, one might think that each surface atom is capable of providing an active site in a surface process but from studies by LEED and flash desorption we know that this is not necessarily the case. The actual surface topology of GaAs ($\bar{1}\bar{1}\bar{1}$) is most complex and is known to be very dependent upon its temperature. In the temperature range at which the desorption experiments were performed it is known that the surface structure is GaAs ($\bar{1}\bar{1}\bar{1}$) $\sqrt{19} \times \sqrt{19} - 23.4^\circ$ (Cho 1970) called a gallium-stabilized surface. At lower temperatures the surface is GaAs ($\bar{1}\bar{1}\bar{1}$) 2×2 , this being termed arsenic-stabilized. Mark (1973) has suggested that both of these surface structures might comply with an electrostatic criterion that at equilibrium the surface must contain $\pm \frac{1}{4}$ of a monolayer of lattice ions. It is thus possible that only one in four surface sites is occupied. Alternately Arthur (1974) has shown that when As is flashed from GaAs ($\bar{1}\bar{1}\bar{1}$) up to half a monolayer can be removed, thus one in two sites could possibly be active. In our calculations on this system we have taken both quarter- and half-monolayer coverage of active sites to represent ρ_s , two resulting d versus a^{-1} curves have been plotted in figure 3. As can be seen for both values of ρ_s the possible halfwidth of one potential decreases drastically as the corresponding equilibrium position of the adatom is moved away from the surface. Taking the value of d to be the bulk near-neighbour separation for GaAs of 2.44 Å, the corresponding values of a^{-1} are found to be unreasonably small for both values of ρ_s .

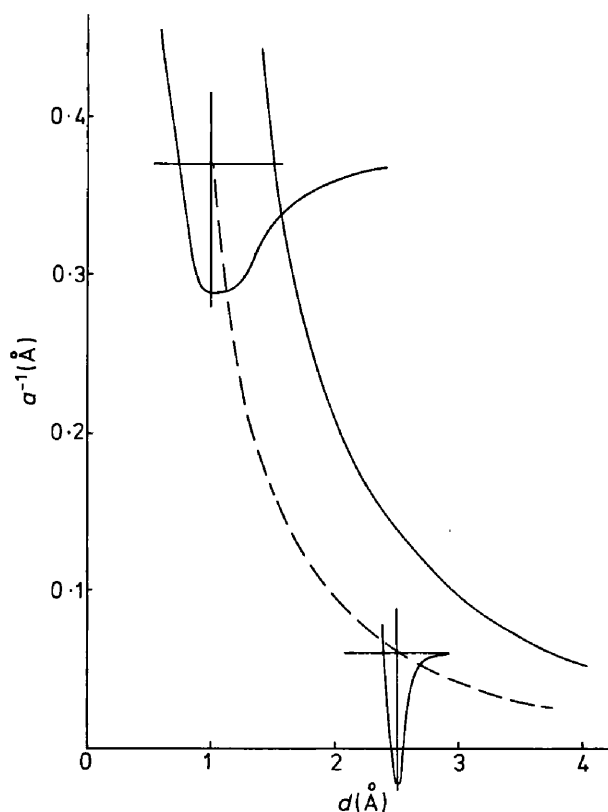


Figure 3. Variation of the potential parameters a^{-1} and d capable of reproducing experimental results for Ga-GaAs ($\bar{1}\bar{1}\bar{1}$): $\rho_s = \frac{1}{4}$ monolayer (solid curve); $\rho_s = \frac{1}{2}$ monolayer (broken curve). Schematic Morse potentials indicate the variation in width as a^{-1} and d change.

It appears from the As–GaAs ($\bar{1}\bar{1}\bar{1}$) parameters evaluated by equation (18) that the desorption process is not well represented. This could be due to the simplicity of the gas–solid potential in that we have assumed bonding to only a single surface site. Bonding to several active sites presents greater difficulty and will not be considered further in this publication. Alternatively, if there was a drastic reduction in the number of active sites on a ($\bar{1}\bar{1}\bar{1}$) face this would increase the width of the potential, although there is no physical evidence suggesting that this is the case. In the calculation we have assumed that the potential is spherically symmetric; as we shall show in the next section, the inclusion of an angular dependence allows a realistic fit to be achieved.

5. Angular-dependent potentials

Gallium arsenide and other III–V compounds crystallize in the zinc blende structure. When cleaved in the $\langle 111 \rangle$ direction, because of the asymmetry of the compound, the ($\bar{1}\bar{1}\bar{1}$) and (111) faces have different atoms exposed. By convention, the (111) or A face contains group III atoms and the ($\bar{1}\bar{1}\bar{1}$) or B face, type V atoms. The bonding of these compounds is predominantly covalent although Phillips (1969) has associated the functional ionicity coefficient with each compound to describe non-covalent forces. The bonding can be understood in terms of sp_3 orbitals and recent tight-binding calculations using only these hybrids have been successful in explaining the surface states on the polar faces of these compounds. The charge density on such a face is extremely localized in lobes situated above the surface atoms; it would appear that a spherically-symmetric potential is not very representative of such a system.

In order to model this interaction it seems plausible to use a potential that is a function of θ as well as r but is independent of ϕ . This model should localize the potential minimum to the volume of space immediately above a surface-active centre. An example of this is

$$U(r) = \frac{1}{2}V(r)(1 + \cos^2 \theta). \quad (21)$$

where θ is the angle between the surface normal and the position vector of the desorbing atom, $V(r)$ is the Morse Potential [equation (6)]. Clearly a detailed examination of this system would merit using a potential designed for GaAs, however, the calculations performed here serve only to indicate the effect of such an inclusion.

Inserting the potential (21) into the general-rate equation (17) and performing the ϕ integration we obtain

$$\tau = \frac{2\pi}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \int_0^\infty dr r^2 \int_0^\pi d\theta \sin \theta \{ \exp[-V(r)(1 + \cos^2 \theta)/k_B T] - 1 \} \quad (22)$$

$$\tau = \frac{4\pi}{r_{ws}^2} (\mu/2\pi k_B T)^{1/2} \int_0^\infty r^2 dr \left\{ \frac{1}{2}(2\pi k_B T/V(r))^{1/2} \operatorname{erf}[(V(r)/2k_B T)] \right. \\ \left. \times \exp(-V(r)/2k_B T) - 1 \right\}. \quad (23)$$

This is the exact expression for the potential of equation (21); however, for low temperatures, if we approximate the error function close to the potential minimum, then Lap-

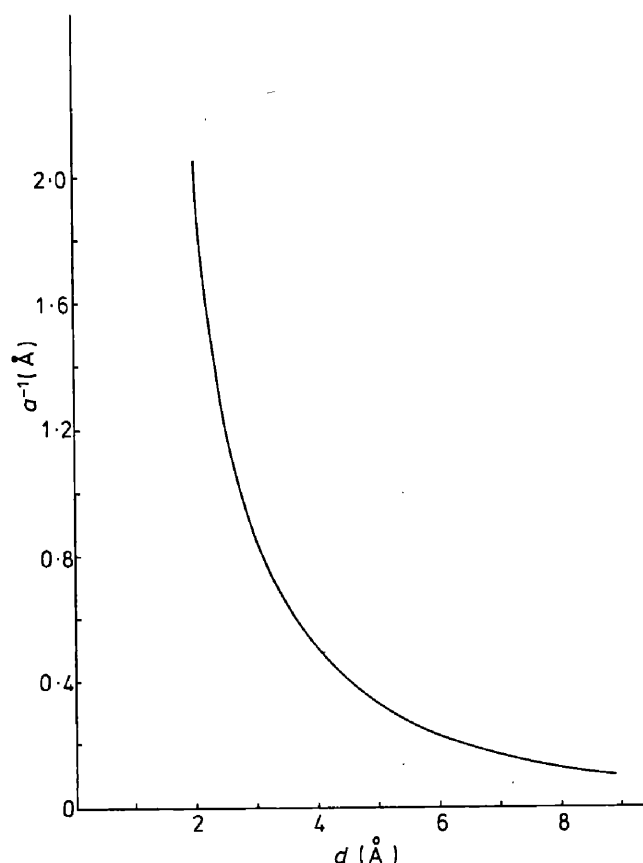


Figure 4. Variation of the potential parameters a^{-1} and d capable of reproducing experimental results for Ga-GaAs (iii) when using an angular-dependent potential.

lace's method may again be employed to evaluate the radial integral to give

$$\tau = \frac{2\pi}{r_{ws}^2} k_B T \frac{[2a^2 d^2 D + (1 - 2a^2 d^2) k_B T] (2\mu)^{1/2}}{2Da^3 (D - k_B T)^{3/2}} \exp(D/k_B T) \quad (24)$$

a result which is accurate to 4%.

Figure 4 shows an a^{-1} versus d curve for the GaAs system where the angular-dependent potential has been used in the delay time equation. The potential halfwidth has considerably increased giving a more realistic value for the Morse interaction, even for a half-monolayer coverage.

6. Low density of active-site limit

A feature of the form of the results, illustrated by equation (17) is the proportionality between the delay time and surface-active site density. This shows that, in the limit of a low density of active sites, the conditions inherent in the formulation are not satisfied. Equation (17) represents the average time delay on the surface. This equals the desorption delay time provided the transfer function, $p(t)$, has an exponential time decay. Experimentally, this function (Jewsbury and Beeby 1975) relates the incident beam flux, $I(t)$, directed onto the surface to the off-going beam flux, $O(t)$, by

$$O(t) = \int_{-\infty}^t dt_1 p(t - t_1) I(t_1);$$

it is always observed to have the required exponential time decay. However, this is strictly only the large time behaviour and it is possible for a significant number of atoms to desorb before $p(t)$ takes on this form. This is the situation when a large number of incident atoms miss the active sites and scatter without appreciable delay.

Thus, invoking a radius of scattering cross section, σ , for the active sites, we might expect

$$p(t) = \left(1 - \frac{\sigma^2}{r_{ws}^2}\right) \Theta(r_{ws} - \sigma) \left(\delta(t - t_0) - \frac{1}{\tau} \exp[-(t - t_0)/\tau] \Theta(t - t_0) \right) + \frac{1}{\tau} \exp[-(t - t_0)/\tau] \Theta(t - t_0)$$

on an experimental time scale. This implies that the average time delay on the surface, $\langle t \rangle$, is

$$\langle t \rangle = \tau \left[1 - \left(1 - \frac{\sigma^2}{r_{ws}^2}\right) \Theta(r_{ws} - \sigma) \right]$$

Thus

$$\tau = \frac{1}{\tilde{\sigma}^2} (\mu/2\pi k_B T)^{1/2} \int dr [\exp(-V(r)/k_B T) - 1]$$

where $\tilde{\sigma}$ is the smaller of σ and r_{ws} .

Now from the work in this paper, we observe that the delay comes predominantly from the region around the potential minimum. This is the reason why the slope of an Arrhenius plot corresponds so closely to the value of the potential minimum, and the reason why a harmonic potential gives such good answers when its parameters are fitted at the bottom of the potential well. The scattering cross section, however, should be more sensitive to the potential away from the minimum but the harmonic fit will give a rough estimate of $\sigma \sim a^{-1} + d$.

Thus, except for exceedingly low densities of surface-active sites, $\tilde{\sigma} = r_{ws}$ and equation (20) approximately represents the delay time.

7. Conclusion and discussion

Numerical calculations have been presented for the rate of desorption from a Morse potential in one dimension using the formulation of Jewsbury and Beeby (1975). The features of the potential that are important in determining the delay time were discussed and it is shown that it is sufficient to use a cut-off harmonic potential when analysing experimental data.

The extension to three dimensions was then made where the modelled system comprises an adatom coupled to only one surface-active site at any time via any potential (the substrate being perfectly general). Numerical calculations using a Morse interaction show that no unique potential satisfies the experimental results. It follows that the equilibrium separation of the adatom-active site pair potential and the corresponding width parameter satisfy a simple relationship. Additional information on these parameters can be obtained from a variety of other experimental techniques, for example LEED or LEIS (Brongersma and Mul 1973) will give overlayer spacings, d , and the selective-adsorption technique of Hoinkes *et al* (1972) which yields the parameters of the gas-

solid potential, $V_{AV}(Z)$, given by

$$V_{AV}(Z) = \frac{1}{A} \int_{\text{unit cell}} dx dy V(x, y, z)$$

where A is the area of the unit cell.

The consequences of allowing an angular dependence in the potential have also been investigated and found to have a significant effect on the delay time.

The final analytic form of the delay time is functionally dependent upon the density of surface-active sites. For all physical values of this density, equation (17) calculates the actual atomic delay time averaged over each of the atoms within the incident beam. For very low values of this density of active sites, however, the delay time as formulated is not the desorption time that is physically measured and we have discussed how our results are related to this experimental value.

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APPENDIX III

The interaction of As₄ and Ga beams on a GaAs (100) surface

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Abstract. A model is proposed to explain the various kinetic processes occurring at a GaAs (100) surface when beams of As₄ and Ga are used to grow GaAs by molecular beam epitaxy. There is a considerable amount of data available on this particular system and an attempt has been made to logically examine the fundamental surface processes and explain them by a semi-empirical model. Reasonable quantitative agreement with experiment, in the temperature range 450–600 K, is achieved for much of the experimental data. One set of experimental results is found to be incompatible with quite general physical arguments. For this reason it is proposed that further experimental work be carried out at exceedingly low Ga fluxes.

1. Introduction

Considerable interest is centred on atom and molecular beam scattering from solid surfaces within the field of chemical physics. The interest stems from a desire to understand the molecule–surface interactions, surface catalysis and also certain technological aspects within the aerospace and semiconductor industries.

Whereas a detailed theoretical understanding of atomic reactions with surfaces is emerging when these interaction times are long (Holloway and Beeby 1975, Jewsbury and Beeby 1975, Holloway and Jewsbury 1976) a corresponding understanding of molecular beam interactions with surfaces does not yet exist. As a result, the interpretation of the interactions involved at a surface has not, in general, been unravelled from the available experimental evidence on such systems.

The purpose of this publication is to present a discussion of some of the processes which may occur when molecular beams are directed onto a surface. The evidence available for one such system is considered with a view to understanding what range of processes dominate a theoretical description. The system chosen involves Ga and As₄ molecular beams interacting on a GaAs (100) surface for which there is a wealth of information published and which also shows many unusual features (Foxon *et al* 1973, 1974, Foxon and Joyce 1975). The impetus for studies of this system arises from attempts to grow high-purity semiconducting films of GaAs by molecular beam epitaxy.

The experimental quantities which characterize this interaction are: (i) sticking coefficient, (ii) accommodation coefficient and (iii) rate of desorption. A thermal beam of As₄ molecules is directed on to the GaAs surface. On arrival at the surface some of the As₄ molecules will fragment or decompose and grow GaAs, this fraction being called the sticking coefficient. The rest of the As₄ molecules will desorb after residing on the surface for an average time of τ —the reciprocal of τ is the rate of desorption. The mean

energy of this desorbing beam is specified by the accommodation coefficient. If the average energy of an impinging As_4 molecule is E_i , of a desorbing molecule is E_0 and of a beam in thermal equilibrium with the surface is E_s , then the accommodation coefficient, α , is

$$\alpha = \frac{E_0 - E_i}{E_s - E_i}. \quad (1)$$

If the beam comes off with the temperature of the surface then $\alpha = 1$ and the beam is said to be fully accommodated.

The experimental measurements of these quantities are reviewed in the next section. In §3 a general description of possible surface events which can explain the qualitative aspects of the results is presented and this is followed in §4 by a quantitative account of this model. Calculations are presented in §5. It is found that one set of experimental results contradicts quite general physical arguments.

2. Experimental observations

The structure of the (100) face of GaAs has been studied by Cho (1971) using RHEED. He found that below 500 K or in the presence of an arsenic beam (As stabilized) the surface had symmetry $c(2 \times 8)$ whereas above 875 K or in the presence of a gallium beam (Ga stabilized) the surface had symmetry $c(8 \times 2)$. Several other structures have been observed in the intermediate temperature range (Cho 1971, Linh 1975, private communication). The experimental evidence (Foxon and Joyce 1975, Arthur 1967, 1974) explains the connection between the supply of a species and the surface temperature in determining the surface structure. Under Langmuir conditions, Ga and As_2 evaporate freely from GaAs; above the congruent temperature of 875 K there is an 'internal source' of Ga arising from the fact that more arsenic than gallium evaporates from the surface.

Experiments are carried out over a range of surface temperatures from 300 to 900 K with both Ga and As stabilized surfaces. Considerable unexplained differences are exhibited in these two situations. In the temperature range 300–450 K, Foxon *et al* (1974) reported delay times τ of

$$\begin{aligned} \tau &= 9.0 \times 10^{-10} \exp(E_d/k_B T) \quad E_d = 0.38 \pm 0.03 \text{ eV: Ga-free surface} \\ \tau &= 1.6 \times 10^{-8} \exp(E_d/k_B T) \quad E_d = 0.36 \pm 0.03 \text{ eV: Ga-exposed surface} \end{aligned} \quad (2)$$

(these values are criticised in §3). The values of the pre-exponential factors are critically dependent upon the surface history, and the desorption energies, E_d , are apparently equal to within experimental error. k_B is Boltzmann's constant and T the surface temperature. Such results can be contrasted with a simple theory of atomic desorption (Beeby and Dobrzynski 1971)

$$\tau = \frac{2\pi}{\bar{\omega}} \exp(E_d/k_B T) \quad (3)$$

where $\bar{\omega}$ is an average adatom surface coupling frequency and should be within two orders of magnitude of $10^{13} \text{ rad s}^{-1}$ and E_d is the binding energy of the adatom to the surface. Pre-exponential factors differing significantly from 10^{-13} s strongly suggest that the actual thermal desorption of the molecules is not the rate-limiting process.

The sticking coefficient of As_4 molecules is zero in the absence of Ga on the surface

and is finite in the presence of Ga. For low Ga fluxes there is a linear relationship of deposited As to Ga, the proportionality continuing approximately until the sticking coefficient reaches about one half. Between 450 and 600 K the sticking coefficient is insensitive to the surface temperature.

The flux of Ga atoms leaving a Knudsen cell is accurately determined by the cell temperature. Unfortunately this is not true in the case of arsenic, where no equilibrium is achieved within the cell between the various evaporating species; thus no reproducibility of arsenic fluxes at specific cell temperatures is attainable. Quoted arsenic fluxes can therefore be at best only guesses and may easily be in error by a factor of 4 up or down. For large enough quantities of As in the cell, however, the flux should remain constant over the time scale of the experiments. If it is assumed that stoichiometric growth of GaAs occurs at low Ga fluxes (as suggested by Foxon and Joyce 1975) then registered arsenic fluxes need to be doubled. In the following work this adjustment has been made to the experimental results.

The reaction orders have also been measured. At high gallium fluxes the reaction is found to be second-order whereas at low gallium fluxes it is first-order. The second-order reaction suggests that at high Ga fluxes, there is a direct or indirect interaction between As₄ molecules or their fragments which dominates the desorption process. From this information we are able to interpret empirically the way an As₄ molecule interacts with the GaAs (100) surface and highlight the complexity of molecule-surface interactions.

3. Surface events

The simplest molecular desorption mechanism corresponds to the molecule adsorbing onto the surface, becoming fully accommodated and bound to the surface at temperature T , where it resides until the random thermal fluctuations provide enough energy to escape. In a simple theoretical description in which the adatom of mass M is bound to a surface atom of mass m by a harmonic well of depth E_B and range x_c , the surface lifetime is given by (Holloway and Beeby 1975)

$$\tau = \pi \left(\frac{2Mmx_c^2}{E_B(M+m)} \right)^{1/2} \exp(E_B/k_B T). \quad (4)$$

Such desorption should be characterized by (i) no sticking, (ii) full thermal accommodation and (iii) a first-order surface reaction—as is the case in the As stabilized regime. The lifetime measurements of Foxon *et al* (1974) are shown in figure 1. A best fit of a straight line through these points yields

$$\tau = 3.8 \times 10^{-10} \exp(E_d/k_B T), \quad E_d = 0.40 \text{ eV}. \quad (5a)$$

Due to the increasing error at higher temperatures, Foxon *et al* weighted against the high-temperature points and obtained $E_d = 0.38 \pm 0.03 \text{ eV}$. However, it should be pointed out that if the highest temperature point is ignored then the best fit straight line through the remaining seven points gives

$$\tau = 3.85 \times 10^{-12} \exp(E_d/k_B T), \quad E_d = 0.53 \text{ eV}. \quad (5b)$$

Consequently, the experimental evidence indicates that E_d is in the range $0.35 < E_d < 0.55 \text{ eV}$. In many ways, equation (5b) looks more reasonable than equation (5a) since the pre-exponential factor is considerably smaller and corresponds to $\bar{\omega} =$

$1.63 \times 10^{12} \text{ rad s}^{-1}$ (equation 3) and $x_c = 7.98 \text{ \AA}$ (equation 4). Thus it is possible that the rate-limiting process for a Ga-free surface is the thermal excitation of the molecule to the gaseous state. Indeed this is what one should expect. Once adsorbed on to the Ga-free surface any hopping from site to site will not influence the delay time; the only mechanisms which could affect the interpretation are (i) fragmentation, (ii) ad-molecule–ad-molecule interactions and (iii) ad-molecule–surface-imperfection interactions. If any fragmentation occurred on the surface we would expect to observe some fragmentation products in the desorbing flux and a finite sticking coefficient—neither of which are observed. Ad-molecule–ad-molecule interactions should also be unimportant since the adsorbing beam fluxes are very low, and evidence that they are unimportant is provided by the observation of first-order reaction kinetics. Ad-molecule–surface-imperfection interactions could, however, have a bearing on the adsorption.

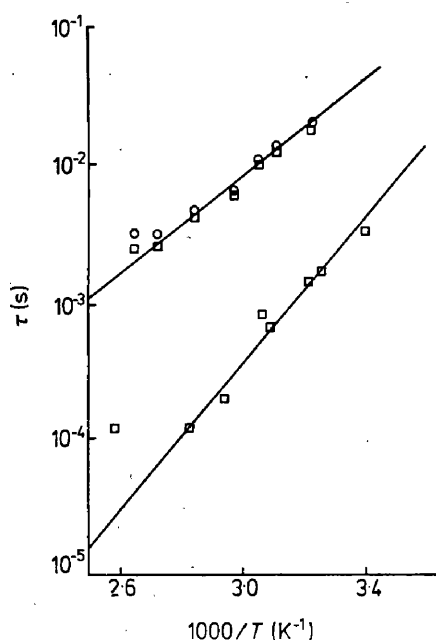


Figure 1. Surface lifetimes of As_4 molecules on Ga- (higher curve) and As- (lower curve) rich GaAs (100) surfaces as a function of temperature.

In the Ga stabilized case with a low flux of As_4 molecules arriving at the surface, the rate-limiting process cannot be the actual thermal desorption of molecules since the pre-exponential factor (2) is too large. Since arsenic atoms bond more strongly to gallium atoms than to arsenic atoms, it is likely that an As_4 molecule will be bound more strongly to a Ga site than to an As site. Since even a small increase in the surface binding energy will increase the surface lifetime by many orders of magnitude, an As_4 is thus unlikely to be capable of desorbing from a Ga site. An As_4 molecule on the surface may (i) hop from site to site, (ii) dissociate to grow GaAs and (iii) desorb. During the surface lifetime of $\sim 10^{-2} \text{ s}$, some of the As_4 molecules will undoubtedly succumb to Ga attack and grow to form GaAs. This will ensure that for small As_4 fluxes a certain fraction of the surface sites, specified by the As_4 impinging flux, will be occupied by As atoms. The migrating As_4 molecule which is unable to escape from the Ga-rich part of the surface may in time reach an As site and thus desorb. In such a situation, the time to desorb (lower line, figure 1) is much less than the total delay time (upper line, figure 1). Thus the rate-limiting process will be the surface migration of an As_4 molecule to an As surface

site—a contention supported by the observation of second-order reaction kinetics at low As₄ impinging fluxes.

4. Model description

The simple picture of surface events described in §3 can readily be transformed into an analytic model if a few further approximations are made. Consider beams of Ga and As₄ with fluxes J_{Ga} and J_{As} molecules cm⁻² s⁻¹ impinging under steady-state conditions onto a GaAs (100) surface. On the experimental time scale every Ga atom can be regarded as sticking wherever it lands on the surface since their lifetimes should be of the order of 10⁶ years (Arthur 1968) at temperatures ~450 K. Only a fraction S of As₄ molecules stick, the remaining fraction eventually desorbing. It is assumed that, when an As₄ molecule dissociates, the As atoms move to sites where they bond to Ga atoms; additional atomic surface mobility is neglected, as is recombination to form As₄ molecules, since As₂ is the natural desorption species. Thus in equilibrium the surface coverage is constant and the rate of 'creation and destruction' of As surface atoms equal; that is

$$4SJ_{\text{As}} = \theta_{\text{As}}J_{\text{Ga}} \quad (6)$$

where θ_{As} is the fractional As coverage. With these approximations, stoichiometric growth of GaAs ($4SJ_{\text{As}} = J_{\text{Ga}}$) is only achieved when $J_{\text{As}} \gg J_{\text{Ga}}$. The dynamics of the As₄ molecule, which for simplicity will be taken to bond to one site at a time, can be described by two probabilities p and f . The first, p , is the average fraction of As₄ molecules bonded to a Ga surface atom which survive migration to an As site without being dissociated, presuming that dissociation can only occur whilst the molecule is bonded to a Ga site. The second, f , represents the fraction of As₄ molecules which having migrated to an As site never again bond to a Ga site. Thus f represents the total fraction of As₄ molecules which desorb from either a particular arsenic surface site or from an arsenic site to which it has hopped, this hopping being only via arsenic sites. Now the As and Ga coverages, θ_{As} and θ_{Ga} ($\theta_{\text{As}} + \theta_{\text{Ga}} = 1$) are taken as representing the ratio of molecules which first land on an As or Ga site, respectively. Thus the fraction of molecules which dissociate can be written as a geometric series which can be summed to

$$S = \theta_{\text{Ga}} \frac{1-p}{1-r} + \theta_{\text{As}} \frac{(1-f)(1-p)}{1-r} \quad (7)$$

where $r = (1-f)p$. These equations can be solved for S and θ_{As} , given p and f , which are determined by the microscopic rate processes.

If τ_{stick} and $\tau_{\text{migration}}$ are the mean sticking and migration times to an As site for an As₄ molecule when on a Ga section of the surface, then the probability of the As₄ molecule surviving t seconds is $\exp(-t/\tau_{\text{stick}})$ and

$$p = \int_0^\infty \frac{dt}{\tau_{\text{migration}}} \exp\left(-\frac{t}{\tau_{\text{migration}}} - \frac{t}{\tau_{\text{stick}}}\right) = \frac{\tau_{\text{stick}}}{\tau_{\text{migration}} + \tau_{\text{stick}}} \quad (8)$$

To simplify the analysis, the pre-exponential factors for hopping, sticking and thermally desorbing will be taken to be equal and where appropriate the coverage will be included to represent the effective coordination of each site. Thus, taking a statistical equilibrium distribution on the surface:

$$f = \frac{\exp(-E_B/k_B T)}{\exp(-E_B/k_B T) + \theta_{Ga} \exp[-(E_{BB} - E_B)/k_B T]} \quad (9)$$

where E_B and E_{BB} are the binding energies of As_4 molecules to As and Ga sites, respectively. Similarly, if Δt is the mean time for one hop, the migration time $\tau_{migration}$ is given by

$$\tau_{migration} = \Delta t \frac{\theta_{As} \exp[-(E_{BB} - E_B)/k_B T] + \theta_{Ga} \exp(-E_H/k_B T)}{\theta_{As} \exp[-(E_{BB} - E_B)/k_B T]} \quad (10)$$

or, using the equality of the pre-exponential factors,

$$\tau_{migration} = \tau_{stick} \{ \theta_{As} \exp[(E_H - E_S)/k_B T] + \theta_{Ga} \exp[(E_{BB} - E_B - E_S)/k_B T] \} / \theta_{As} \quad (11)$$

Here E_H and E_S are the activation energies for hopping and sticking, respectively. Hence the sticking coefficient and coverage are given by the solution of the implicit equation

$$S = \frac{1-p}{1-r} (1 - f \theta_{As}) = \frac{1}{4} \theta_{As} q \quad (12)$$

where $q = J_{Ga}/J_{As}$. This expression only involves the four activation energies E_B , E_{BB} , E_H and E_S , the temperature and the impinging beam flux ratio.

When q is small, the sticking coefficient is small and hence the desorbing flux of As_4 molecules, $J_{As}^{(0)}$, is approximately equal to the impinging flux, which implies that the interaction is first-order. On the other hand, at large q values,

$$S = \frac{1-p}{1-r} = 1 - \frac{pf}{1-r}.$$

p is very small and hence

$$J_{As}^{(0)} = J_{As}(1 - S) \simeq J_{As} \frac{\tau_{stick} f}{\tau_{migration}}.$$

On reorganising we find that the interaction is second-order, that is

$$J_{As}^{(0)} = 4 \frac{\tau_{stick} f}{\tau_{transfer}} \frac{J_{As}^2}{J_{Ga}} \quad (13)$$

Here $\tau_{transfer}$ is the mean time required to jump from a Ga site to an As site:

$$\tau_{transfer} = \frac{2\pi}{\omega} \exp[(E_{BB} - E_B)/k_B T]. \quad (14)$$

An expression for the total delay time, τ_{delay} , on the surface can also be derived. Let τ_B be the desorption time for a totally As covered surface; that is

$$\tau_B = \frac{2\pi}{\omega} \exp(E_B/k_B T). \quad (15)$$

Then τ_{delay} can be derived in a similar manner to that used for equation (7):

$$\tau_{delay} = \theta_{Ga} \left(\frac{\tau_{migration} + 2\tau_{transfer}}{1-r} + \tau_B - \tau_{transfer} \right) + \theta_{As} \left(\tau_B + \frac{p(1-f)(\tau_{migration} + 2\tau_{transfer})}{1-r} \right).$$

This can be written as

$$\tau_{\text{delay}} = \tau_B + (\tau_{\text{migration}} + 2\tau_{\text{transfer}}) \left(\frac{1}{1-r} - \theta_{\text{As}} \right) - \theta_{\text{Ga}} \tau_{\text{transfer}}, \quad (16)$$

For high Ga coverages $\tau_{\text{delay}} = \tau_{\text{migration}} + \tau_{\text{transfer}} + \tau_B$, and if $E_{\text{BB}} < 2E_B$ then the rate limiting process is the surface migration and $\tau_{\text{delay}} \approx \tau_{\text{migration}}$. Hence the Arrhenius plot (figure 1) suggests that $E_{\text{BB}} - E_B = 0.36$ eV. At high As coverages we obtain $\tau_{\text{delay}} = \tau_B$. Taking equation (5b) to be a rough estimate for the delay time, we obtain $E_B \approx 0.53$ eV.

5. Comparison with experiment

The analysis presented in §4 is for a steady-state situation. The experiments, however, are performed by modulating the As₄ impinging flux. Fortunately, with As₄ beam fluxes up to 10^{13} molecules cm⁻² s⁻¹ and chopping frequencies greater than 25 Hz, less than 2×10^{11} molecules cm⁻² arrive at the surface during one period (a typical surface contains 10^{15} atoms cm⁻²). Thus, after a periodic response has been achieved, As₄ deposited during one half-period cannot effectively change the surface concentration and we can view the experiments as being carried out under conditions of constant surface coverage.

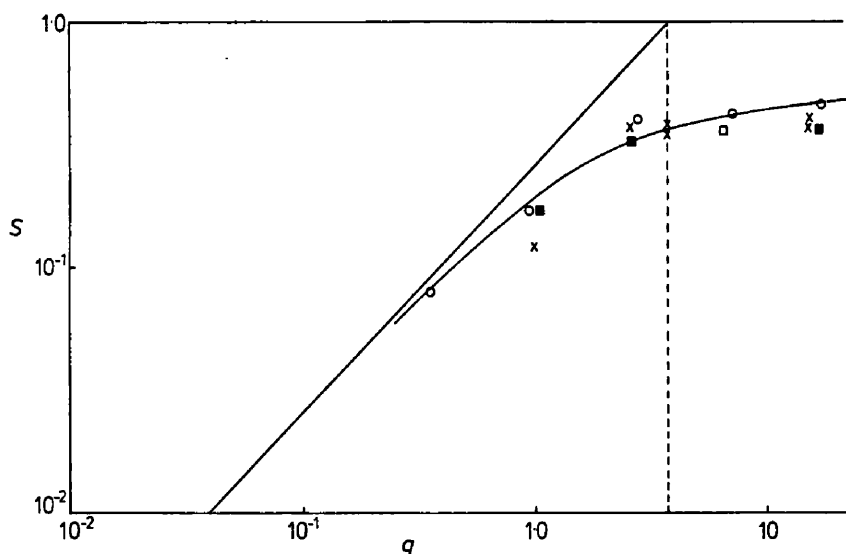


Figure 2. The sticking coefficient of As₄ as a function of the mean flux ratio q in the temperature range 450–600 K with a modulated As₄ impinging flux of 9×10^{12} molecules cm⁻² s⁻¹. The experimental points labelled O, x, □ agree well with the theoretical curve (full line). Also shown is a one atom of As to one atom of Ga sticking line ($S = \frac{1}{4}q$) and the dividing line (dotted) between excess Ga and As arriving at the surface.

Arsenic fluxes were adjusted as discussed in §2. The activation energies were varied and solutions found for S versus q (figure 2) in good agreement with the experimental values. Sets of values of the energies giving this fit are shown in table 1. The equations are such that the sticking coefficient is, in fact, determined by just the three energy differences $2E_B - E_{\text{BB}}$, $E_H - E_B$ and $E_S - E_B$. Values which fit the experimental results satisfy the relationships

$$E_{\text{BB}} - 2E_{\text{B}} + E_{\text{S}} - E_{\text{H}} \simeq 0$$

$$E_{\text{H}} + E_{\text{B}} - E_{\text{BB}} > 3 \times 10^{-13} \text{ ergs} \sim 5 k_{\text{B}} T \quad (17)$$

and these conditions also automatically ensure that the sticking coefficient is insensitive to the surface temperature in the range 450–600 K. Thus no unique solution is specified by the experimental results. The standard deviation of points scattered about this line corresponds to an error $\sim 15\%$.

Table 1. Values for activation energies (in ergs) of As_4 molecules for hopping, E_{H} , sticking, E_{S} , and bonding to As, E_{B} , and Ga, E_{BB} , active sites, which produce the fit to experiment shown in figure 1.

E_{H} ($\times 10^{-13}$)	E_{S} ($\times 10^{-12}$)	E_{B} ($\times 10^{-13}$)	E_{BB} ($\times 10^{-12}$)
10.0	1.27	8.44	1.42
12.0	1.47	8.44	1.42
8.0	1.292	8.44	1.2
10.0	1.492	8.44	1.2
5.77	1.27	8.44	1.0

The derivative of the off-going As_4 flux has also been measured by using a three-beam technique—unmodulated Ga and As_4 beams and a smaller, modulated, As_4 beam. As discussed at the start of this section, the modulated beam represents a small perturbation from the equilibrium situation, so that in terms of the steady-state relationships the derivative of the off-going As_4 flux, H_{S} , is just

$$H_{\text{S}} = \left(\frac{\partial J_{\text{As}}^{(0)}}{\partial J_{\text{As}}} \right)_{\theta_{\text{As}}} = (1 - S). \quad (18)$$

This result, however, is apparently contradicted by the experimental results since they show values of $H_{\text{S}} > 1$ (figure 3). In order to justify equation (18), the time-dependent problem has been considered. The surface response time ($\sim$ desorption time, sticking

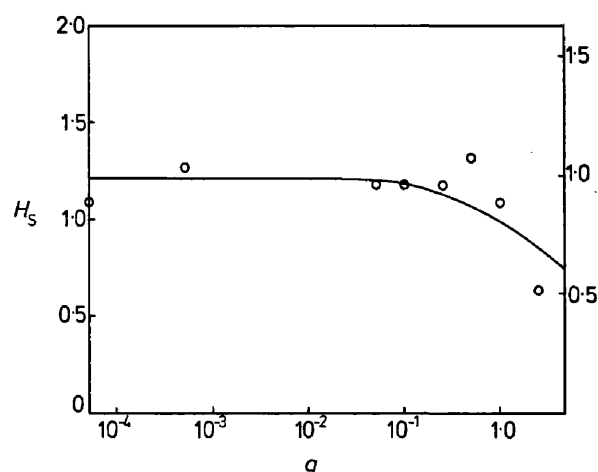


Figure 3. Derivative of offgoing flux (equation 18) as a function of the flux ratio at a surface temperature of 545 K and an incident unmodulated As_4 flux of 2×10^{13} molecules $\text{cm}^{-2} \text{ s}^{-1}$. Experimental points refer to the left-hand scale and the theoretical curve to the right-hand scale.

time etc) is very fast on the time scale of the chopping—experiment places an upper limit of 10^4 s. Hence equation (6) becomes

$$\rho \frac{d\theta_{\text{As}}}{dt} = 4S(\theta_{\text{As}}) J_{\text{As}}(t) - \theta_{\text{As}} J_{\text{Ga}} \quad (19)$$

where ρ is the surface density of atomic sites, $J_{\text{As}}(t)$ the time-dependent incident flux of As₄ molecules, and $S(\theta_{\text{As}})$ the sticking coefficient as a function of $\theta_{\text{As}}(t)$ given by equation (7). Calculations revealed that with a chopping frequency of 1570 rad s^{-1} , a gallium flux of $7.8 \times 10^{13} \text{ molecules cm}^{-2} \text{ s}^{-1}$, an unmodulated arsenic flux of $2.0 \times 10^{13} \text{ molecules cm}^{-2} \text{ s}^{-1}$ and a modulated arsenic flux of $1.7 \times 10^{12} \text{ molecules cm}^{-2} \text{ s}^{-1}$, only small variations in the sixth decimal place of the sticking coefficient were produced. Thus the constant coverage assertion of equation (18) is fully justified.

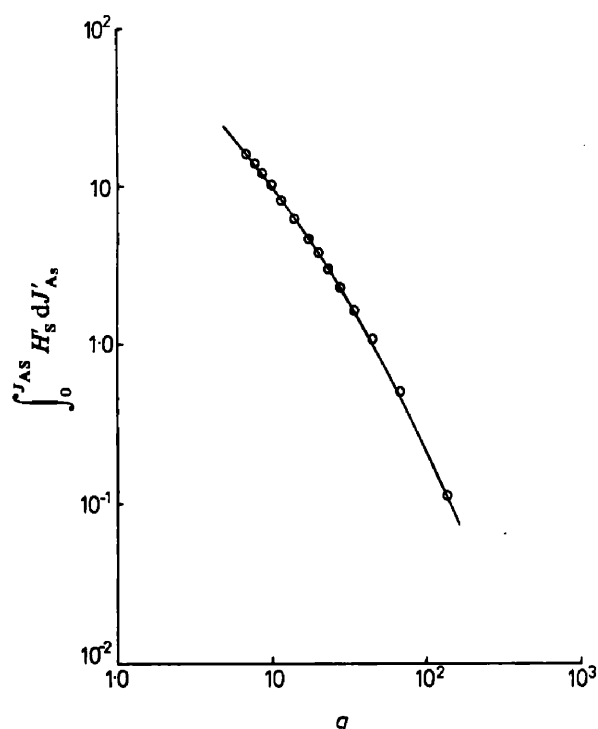


Figure 4. Integral of H_s at a surface temperature of 550 K and constant impinging Ga flux of $6.6 \times 10^{13} \text{ atoms cm}^{-2} \text{ s}^{-1}$. If the surface rapidly re-equilibrates during modulation of the As₄ beam, then this is the desorbing As₄ flux.

The only way that H_s can be reasonably greater than unity is for the surface to rapidly re-equilibrate; that is, the incident fluxes are sufficiently large that the surface moves rapidly to a new equilibrium as the arsenic flux is modulated. This is the opposite extreme to the situation just discussed and could apply, for instance, if the surface density of bonding sites were several orders of magnitude less than expected. In this situation

$$H_s = \frac{dJ_{\text{As}}^{(0)}}{dJ_{\text{As}}} = (1 - S) + q \frac{d}{dq} S(q). \quad (20)$$

Furthermore, it is then meaningful to integrate over J_{As} to obtain $J_{\text{As}}^{(0)}$ (figure 4):

$$J_{\text{As}}^{(0)} = \int_0^{J_{\text{As}}} H'_s dJ_{\text{As}} = J_{\text{As}} q \int_q^\infty H_s(q_1) \frac{dq_1}{q_1^2}. \quad (21)$$

The slope of $J_{\text{As}}^{(0)}$ versus J_{As} gives the reaction order, R :

$$R = \frac{d(\ln J_{\text{As}}^{(0)})}{d(\ln J_{\text{As}})} = \frac{H_s}{1 - S}. \quad (22)$$

It can be seen that if the sticking coefficient is just a function of q , even this interpretation is incompatible with the experimental results in figures 2, 3 and 4. For instance, the condition $H_s > 1$ is just $dS/dq > S/q$ or $(R - 1)/R > S$. At $q = 10$, $R = 1.3$ and then $H > 1$ but S is not less than 0.23. Similarly, since the reaction order is always less than 2, $H_s > 1$ cannot occur unless $S < \frac{1}{2}$. Furthermore, there is a limit to the range of q values over which $H_s > 1$ is allowed. From equation (21), observe

$$S(q) = -q \int_q^\infty \frac{H_s(q_1) - 1}{q_1^2} dq_1. \quad (23)$$

If $H_s(q_0)$ is approximately constant and greater than unity in the range $q_1 < q_0 < q_2$, then

$$q_2 S(q_1) - q_1 S(q_2) = (H_s - 1)(q_1 - q_2).$$

Since $S(q_1) > 0$ and $S(q_2) < \frac{1}{2}$ it follows that

$$1 > 2(H_s - 1) \left(\frac{q_2}{q_1} - 1 \right). \quad (24)$$

This inequality arises from the physical bounds on $S(q)$. Hence if $(H_s - 1)$ is constant between $q = 10^{-4}$ and $q = 10^{-1}$, then $H_s < 1.0005$. The result (24) is still valid even if S is not solely a function of q provided $J_{\text{Ga}} = \text{constant}$ and $q_2/q_1 = J_{\text{As}}^{(1)}/J_{\text{As}}^{(2)}$ —however, in this case, comparison with experiment is not possible since figure 3 refers to a variable Ga flux.

Experimentally, H_s is difficult to measure and has to be normalized so that $H_s(q = 0) = 1$. If this value is assumed to have been incorrectly assigned, reasonable agreement between experiment and theory (equations (18) and (17)) can be achieved (figure 3). Over the range $10^{-4} < q < 10^{-1}$ H_s is remarkably constant and close to the theoretically assumed unit value. Experiment measures a definite and rapid 20% drop from this value to $q \simeq 0$.

If this is a real surface effect, then it demonstrates that a small number of Ga atoms can have a quite disproportionate and unexpected effect on the surface response. This effect is possibly the most important aspect of all the experimental measurements.

In the analysis presented here, we have assumed that at low Ga fluxes, stoichiometric growth of GaAs occurs. No description of the molecular dissociation and surface formation was given—it was only necessary to assume that bonding to a Ga site was required to initiate the dissociation which, once started, would go to completion and that free roving As atoms would always be able to find Ga atoms and grow GaAs. Clearly this is unsatisfactory when the Ga flux becomes exceedingly low and the details of the growth then become important.

6. Discussion

In this paper we have attempted to formulate a qualitative and empirical description of the kinetics of the interaction between As_4 and Ga beams on a GaAs (100) surface. The experimental data are recent and the experiments themselves are very difficult to perform.

Satisfactory agreement between experiment and a three-parameter model was achieved in the temperature range 450–600 K by imposing two restraints on these parameters.

As pointed out by Foxon and Joyce (1975), data in the ranges 300–450 K and 600–900 K indicate that different processes occur in these regimes. It seems likely (Foxon and Joyce 1975) that above 600 K there is effectively a supply of Ga to the surface from the bulk (probably by As₂ evaporation), but below 450 K less data are available and the authors of this paper do not hazard a guess as to its explanation, beyond the comments on the delay times (figure 1).

The description of the surface events in the temperature range 450–600 K, if wrong, could be easily disproven by further experiments. It is hoped that this paper will prompt further work in this field.

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INSTRUMENT RESPONSE FUNCTION OF A QUADRUPOLE MASS SPECTROMETER USED IN TIME-OF-FLIGHT MEASUREMENTS

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ABSTRACT

It is usually assumed that a quadrupole mass spectrometer with a cross-beam ionizer acts as an ideal density-sensitive detector. It is shown that this is not the case, with the result that measured velocity distributions are in error owing to an instrument response which is a strong function of several operating parameters. Further complications are introduced if the parent molecule undergoes fragmentation in the ionizer. Results for As_4 and Pb neutral beams are used to illustrate detector behaviour with and without fragmentation, respectively. Some consideration is also given to improved forms of signal processing and analysis of time-of-flight data.

INTRODUCTION

Time-of-flight (TOF) measurements provide a valuable means of velocity analysis of molecular beams and of fluxes desorbing from or being scattered by surfaces. The principle is very simple: a pulse of molecules is periodically transmitted by a rotating disc in which there is a narrow slit. The period between successive pulses is divided into a large number of short time-intervals, so that all molecules travelling from the chopper disc to a detector are counted as single particles in the time channel which corresponds to their arrival time. A time-zero for each period is established by means of a synchronization pulse derived from the chopper disc and the sequence is repeated for many periods until an adequate count is accumulated in each channel. The technique has already been described in considerable detail by several authors (e.g. [1–5]) so the description need not be repeated here.

The main point which is considered in this paper concerns the behaviour of a particular type of detector very commonly used in TOF measurements, namely a quadrupole resonance mass spectrometer with a cross-beam ionizer. It is normally assumed that such a device acts as an ideal density-sensitive detector, but it is shown that this is not the case, with the result that measured velocity distributions are in error owing to an instrument response which is a strong function of several operating parameters. Further complications are introduced if the parent molecule undergoes fragmentation in the mass spectrometer. A second aspect covered concerns improved signal-processing techniques for TOF data.

This investigation arose out of an attempt to measure energy-exchange processes occurring when beams of As_4 and Ga were incident on a single-crystal GaAs substrate, by modulating the desorbed products and carrying out a TOF analysis. The results of a similar investigation have been published by Arthur and Brown [6]. In addition TOF analysis has been proposed by Farrow [7] as a technique for assigning ion currents detected in the mass spectra of molecular beams, with particular reference to III-V compounds. The results reported here enable the reliability of this application of TOF analysis to be examined critically.

EXPERIMENTAL

The UHV system, beam source, modulator, detector, data-acquisition and signal-processing details have been published previously [8]; only those features which are essential to the present work will therefore be described here. The detector was an EAI Quad 1100, used with the ionizer in the cross-beam mode, and having a liquid-nitrogen-cooled surface surrounding it, so that molecules passing through without being ionized were condensed and not scattered back. Beams of Sb_4 , As_4 , As_2 , Ga, Mg, Pb, and Zn were formed from semiconductor-grade material, with unmodulated intensities at the detector in the range 10^8 – 10^{14} molecules $\text{cm}^{-2} \text{ s}^{-1}$. The Knudsen cell had a slit-width of 0.1 mm, and the equilibrium vapour pressure of the materials used, determined by effusive flux-intensity measurements, agreed well with published data when a direct calibration of intensity with respect to the mass-spectrometer signal was possible (for Ga, Mg, Pb, and Zn). The cell had direct line-of-sight of the mass spectrometer, with a cell-to-modulator distance of 12.8 cm, and a modulator-to-detector spacing of 21.5 cm. The beams were modulated by a thin rotating disc driven by a bakeable synchronous motor (Ferranti model AER/9B). The disc had a diameter of 8.0 cm, with two slits 180° apart and 1.0 mm wide which produced pulses of duration comparable to the sampling interval. Some experiments were also performed with a sectorised disc which produced a pulse train having a mark-space ratio of unity.

Ions were produced from the molecular beams by electron-impact ionization, and after mass filtering those arriving at the electron-multiplier stage of the mass spectrometer were counted using a charge-sensitive preamplifier and discriminator, which was set at a level to eliminate photon noise and other spurious events. The ion arrival rate was recorded in a computer-simulated multichannel scaler having a minimum channel advance rate of $50 \mu\text{s}$ per channel and a dead time of $< 0.1 \mu\text{s}$ per channel. The complete recording system was driven by one quartz crystal oscillator, which produced a pulse train at the sampling frequency. This was divided down to give a synchronizing pulse, such that there were 2^n sampling pulses per synchronization pulse. The motor was phase locked to the synchronizing pulse, so that on average there were 2^{n+1} pulses per revolution. In order to measure the stability of the system an optical reference pulse was generated internally by a lamp and phototransistor placed on opposite sides of the disc, and the channel in which this pulse occurred was recorded. A histogram was thus developed from sequential revolutions which indicated the number of channels over which the pulse occurred. In an ideal situation of complete stability, therefore, the light pulse would always occur in the same channel; in practice this was true for $n \leq 9$.

BASIC THEORY OF TOF SPECTRA

For a group of molecules effusing from a Knudsen cell, the Maxwell-Boltzmann distribution function $\Phi(v)$, having dimensions $L^{-1} T$, permits the calculation of the fraction of molecules dN/N , passing a point in space with velocities between v and $v+dv$, i.e.

$$\left. \frac{dN}{N} \right|_v = \Phi(v)dv = 2\beta^4 v^3 \exp(-\beta^2 v^2) dv \quad (1)$$

where

$$\beta^2 = m/2kT \quad (2)$$

in which m is the mass of the molecules and T the absolute temperature of the source.

This can be transferred to a TOF distribution to give the number of molecules travelling a distance L in the time interval between t and $t+dt$, having all set out at $t=0$. Let $F(t)$ be the distribution in the time domain corresponding to the velocity distribution $\Phi(v)$. Then since the total number of particles in each distribution must be the same, it follows that

$$\Phi(v)dv = F(t)dt \quad (3)$$

or

$$F(t) = \Phi(v) \frac{dv}{dt} \quad (4)$$

but since $v = \frac{L}{t}$,

$$F(t) = \Phi\left(\frac{L}{t}\right) \times -\frac{L}{t^2} \quad (5)$$

where the minus sign is introduced because increasing times correspond to decreasing velocities.

Therefore from eqns. (1) and (5)

$$\frac{dN}{N}\bigg|_t = F(t)dt = 2\beta^4 \frac{L^4}{t^5} \exp(-\beta^2 L^2/t^2)dt \quad (6)$$

If all the molecules pass through an ionizer at the distance L , the time-dependent number density ($\rho(t)$) between t and $t+dt$ in the ionizer is obtained by dividing $F(t)$ by the velocity (L/t) so that

$$\rho(t) = 4(\pi)^{-\frac{1}{2}} \frac{\beta^3 L^3}{t^4} \exp(-\beta^2 L^2/t^2) \quad (7)$$

where $4(\pi)^{-\frac{1}{2}}$ is a normalizing constant introduced to keep $\int_0^\infty \rho(t)dt = 1$. This basic theory has also been discussed in previous work (e.g. [1, 3, 4]).

Equation (7) is the expression used in evaluating experimental data to generate the flight time distribution, and it is clear that it contains an implicit assumption that the ionizer is behaving as an ideal density detector.

DATA ANALYSIS

Two basic modulation techniques are used in TOF experiments; in the first a modulator with a very narrow slot produces an opening time which is short compared to the molecular flight time; this will be referred to as delta-function modulation. Alternatively, a much broader slot can be used, in which case the so-called shutter function (i.e. the fraction of the total number of molecules in the pulse being transmitted by the modulator as a function of the pulse duration) must be deconvolved from the time-dependent number-density function given by eqn. (7). Clearly, the former method is more satisfactory, but it can only be used if the unmodulated beam intensity and the detector sensitivity are both reasonably high, because there is a very large intensity loss at the narrow slot modulator. For surface-scattering experiments particularly, the intensity is too low to use delta-function modulation, so the deconvolution approach must be adopted. Data-analysis techniques for both methods are described below.

Delta-function modulation

The method is most easily considered by reference to Fig. 1(a), which represents the form of signal presentation. It is first necessary to establish a time

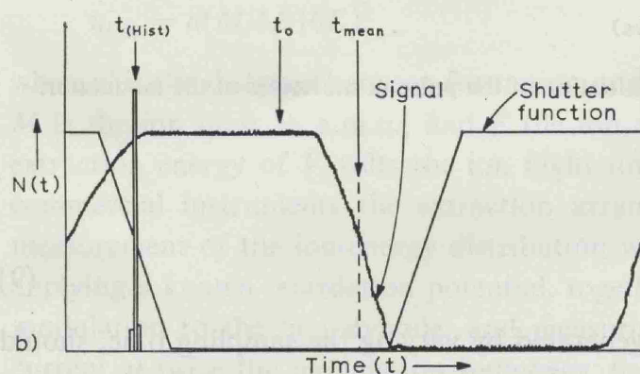
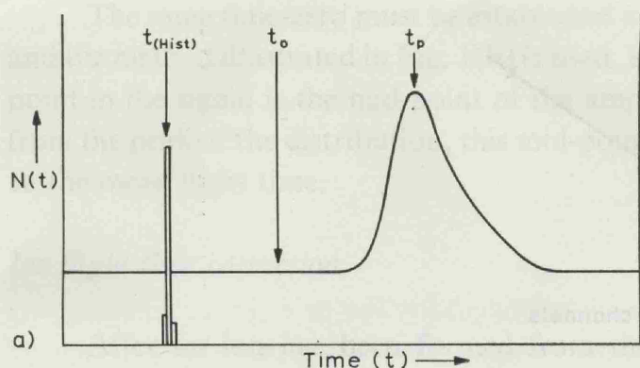


Fig. 1. Signal presentation and timing sequence for TOF data. (a) Delta-function modulation; (b) broad-shutter function.

zero, t_0 , i.e. the point in the scan at which the molecules set off from the modulator. The recorded points are t_{HIST} , which is the histogram channel, corresponding to the time when the light beam was interrupted by the modulator, and t_p , the time to the peak of the distribution.

Now

$$t_p - t_{\text{HIST}} = t_1 + t_2 + t_4 = t_3 \quad (8)$$

where

t_1 = time between modulation of the light beam and modulation of the molecular beam;

t_2 = molecular flight time = $t_p - t_0$;

and

t_4 = ion flight time (which will be discussed later).

But

$t_1 = n\Delta t$, where n is the number of channels (not necessarily integral) between modulation of the light beam and the molecular beam, and Δt is the time

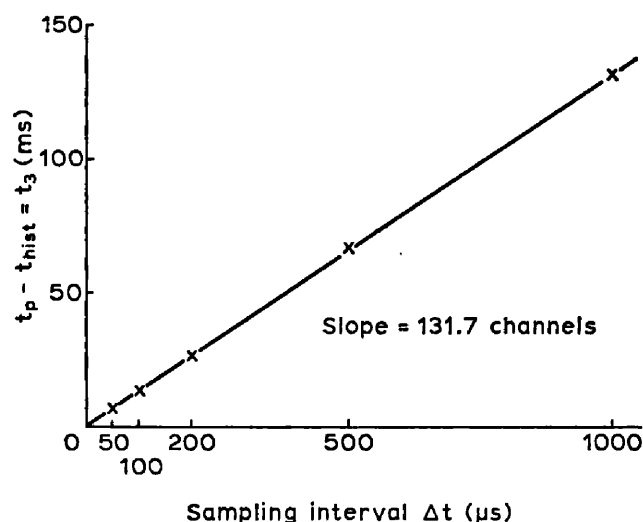


Fig. 2. Derivation of time-zero, t_0 , for initiation of the pulse of molecules at the modulator.

per channel. Therefore

$$t_3 = n\Delta t + t_2 + t_4 \quad (9)$$

A plot of t_3 as a function of Δt , generated by varying the sampling time, should therefore yield a straight line having a slope of n and an intercept corresponding to the time of flight. A typical set of experimental data is shown in Fig. 2. The important point is that n is evaluated accurately (to ± 0.3 of a channel) so that t_0 is precisely established, and a complete TOF spectrum can be obtained. The mean TOF value determined from the intercept is only approximate, and the more detailed evaluation actually used will be described later.

Deconvolution of the shutter function

For the situation where the shutter opening is no longer short by comparison with the molecular flight time, the signal is a convolution of the shutter function and the time-dependent number-density function. The deconvolution is best performed in the frequency domain, using Fourier-transform techniques [8], since the convolution integral becomes a simple product in this representation.

$$\text{i.e. } S(f) = \rho(f) \times G(f) \quad (10)$$

where $S(f)$ is the Fourier transform of the detected signal, $\rho(f)$ is the Fourier transform of the measured molecular flight time and $G(f)$ is the Fourier transform of the shutter function. To compare the measured time-of-flight distribution with the theoretical distribution, the frequency-dependent phase shift $\Delta\Phi$ of $\rho(f)$ is compared with the frequency-dependent phase shift calculated from the Fourier transform of eqn. (7) [9].

The same time-zero must be established as with the delta-function approach, and the method illustrated in Fig. 1(b) is used. Here the most easily characterizable point in the signal is the mid-point of the amplitude, so instead of calculating t_0 from the peak of the distribution, this mid-point is used, which in fact corresponds to the mean flight time.

Ion flight time correction

After an ion has been formed from the parent molecule, it must travel through the quadrupole lens of the mass spectrometer to the first dynode. To a first approximation the time taken, t_{ION} , is a function of ion energy and is given by

$$t_{\text{ION}} = d(M/1.916E)^{\frac{1}{2}} \quad (11)$$

where d is the distance between formation and detection (15 ± 1 cm in this case), M is the ion mass in a.m.u., and E the ion energy in eV. Thus for a nominal extraction energy of V volts the ion flight time can be calculated. However, in commercial instruments the extraction arrangement is not ideal, so a direct measurement of the ion-energy distribution was made. This was carried out by applying a known retardation potential, together with a small superimposed a.c. modulation to the first dynode, and measuring the a.c. component of the ion current at twice the modulation frequency, to give $dN(E)/dE$ as the retardation potential was ramped. The result is shown in Fig. 3, and clearly indicates that the maximum ion energy is the same as the extraction voltage applied, but the mean

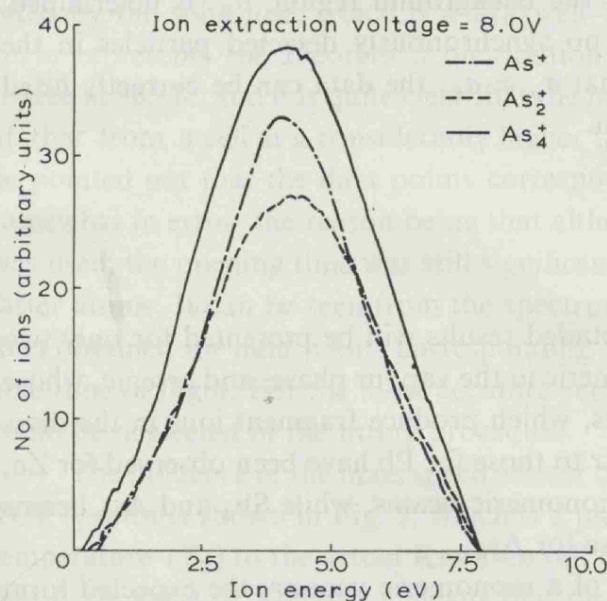


Fig. 3. Measured ion-energy distribution at the first dynode of the mass-spectrometer electron multiplier.

energy is significantly less (by almost a factor of two). The calculated values of ion transit time used in this paper were obtained from this distribution data. Errors in beam-temperature determination of up to 30 K can arise as a result of neglecting this correction.

Data treatment

The final theoretical point to be considered is the best means of analysing the measured TOF spectrum in order to calculate the effective temperature of the beam source (either Knudsen cell or scattering surface). The most accurate method is to fit the measured data to a theoretical Maxwell–Boltzmann distribution, whose functional form is given by eqn. (7). In the measured data, however, there are three parameters which must be optimized in order to be able to fit the correct form of the theoretical distribution to these measurements. These parameters are (i) the background count rate in the mass spectrometer (typically 100 s^{-1}) which is not time-related with respect to the beam modulation, (ii) the total number of synchronously detected particles counted, i.e. the area under the experimental curve, after removal of the background counts, and (iii) the effective source temperature. The fitting procedure used was a damped least-squares method [10], which produces an optimum fit of the experimental data to a Maxwell–Boltzmann distribution, from which the effective source temperature can be calculated simply.

In order to check that the actual data can be properly fitted to a Maxwell–Boltzmann distribution the following statistical test is performed. First the standard deviation, σ_p , of the measured distribution with respect to the theoretical Maxwell–Boltzmann function is determined in the region of the peak. Then the corresponding standard deviation in the background region, σ_B , is determined, with the assumption that there are no synchronously detected particles in the background count. Then provided that $\sigma_p \approx \sigma_B$, the data can be correctly fitted by a Maxwell–Boltzmann distribution.

RESULTS

For the sake of conciseness, detailed results will be presented for only two elements, Pb, which is entirely monomeric in the vapour phase, and arsenic, whose vapour is composed of As_4 molecules, which produce fragment ions in the mass spectrometer. However, results similar to those for Pb have been observed for Zn, Ga, and Mg, all of which produce monomeric beams, while Sb_4 and As_2 beams gave results closely analogous to those for As_4 .

Consider first the simpler case of a monomeric vapour; the expected form of the TOF spectrum is clearly a Maxwell–Boltzmann distribution as given by eqn. (7). In practice, the data could always be fitted to an expression of this form,

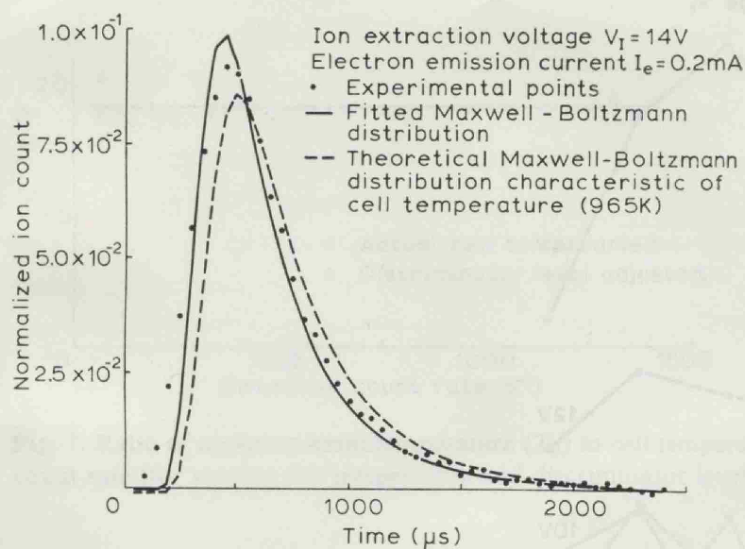


Fig. 4. Time-of-flight spectrum for lead.

but it was found that cell temperatures calculated from the experimental spectra differed significantly from measured cell temperatures, the differences being strongly dependent on several operating parameters of the mass spectrometer. These were (a) the ion-extraction voltage, V_I , (b) the electron-emission current, I_e , and (c) the geometry of the entrance aperture for the neutral beam into the ionizer.

Figure 4 shows a typical set of data for Pb obtained from a beam produced from a Knudsen cell at a temperature of 965 K. The points represent the measured ion count as a function of time, i.e. the flight time distribution, and these are well fitted by the solid line, which is a Maxwell-Boltzmann distribution. The dotted curve represents the theoretical distribution which would be produced from a source at 965 K, and it is quite clear that the measured distribution is characteristic of that from a cell at a considerably higher temperature (1247 K in fact). It must be pointed out that the data points corresponding to the shorter flight times are somewhat in error, the reason being that although a very narrow shutter function was used, the opening time was still significant compared to the flight times of the faster atoms. It can be seen from the spectrum, however, that an extremely good fit is obtained for data points corresponding to times greater than the most probable time of flight. For the most accurate representation, the first few data points could be neglected in the fitting procedure.

The influence of the mass spectrometer operating conditions on the measured TOF spectra is shown in Fig. 5, which is a plot of the ratio of the apparent beam temperature (T_B) to the actual Knudsen cell temperature (T_F), as a function of V_I and I_e . A value of $T_B/T_F = 1$ means that the cell temperature as measured from the TOF spectrum is equal to the actual cell temperature. It is clear that both V_I and I_e have a very strong influence on T_B/T_F , and that $T_B > T_F$ under most condi-

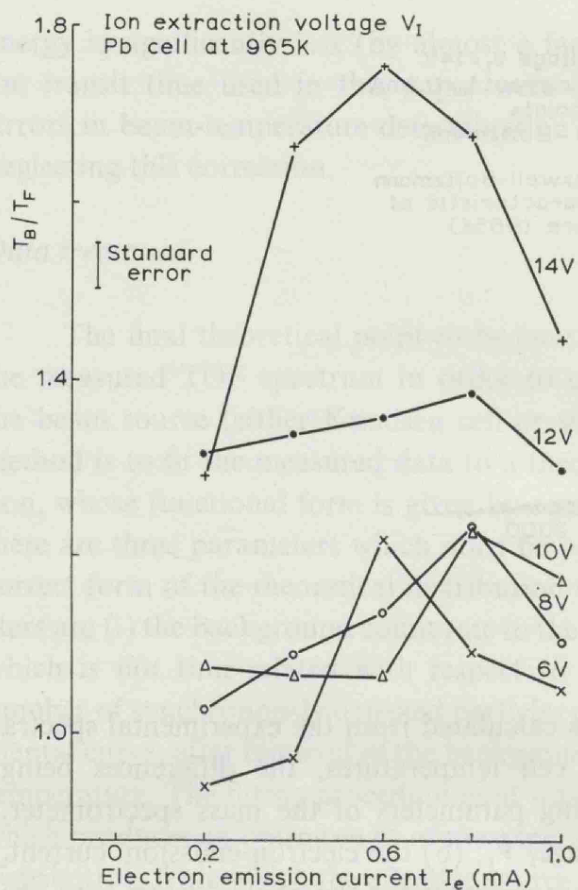


Fig. 5. Ratio of apparent beam temperature (T_B) to cell temperature (T_F) as a function of emission current and ion-extraction voltage.

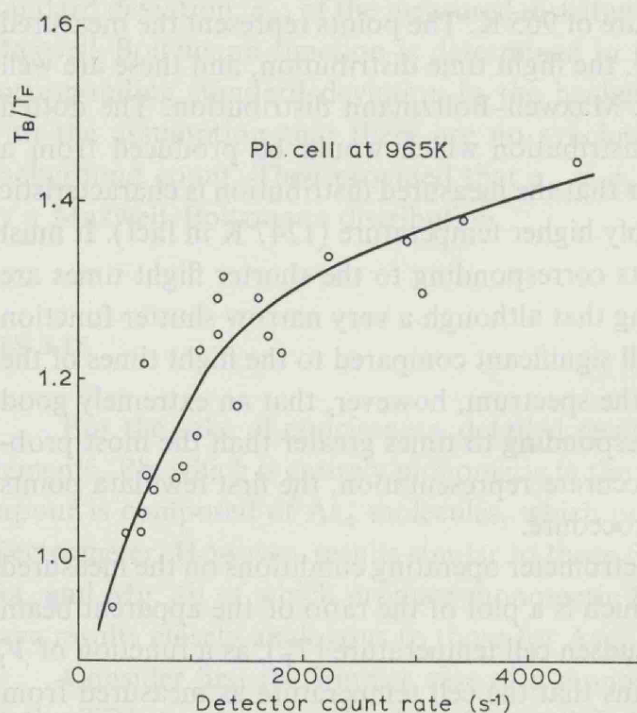


Fig. 6. Ratio of apparent beam temperature (T_B) to cell temperature (T_F) as a function of detector count rate (for varying V_I and I_e).

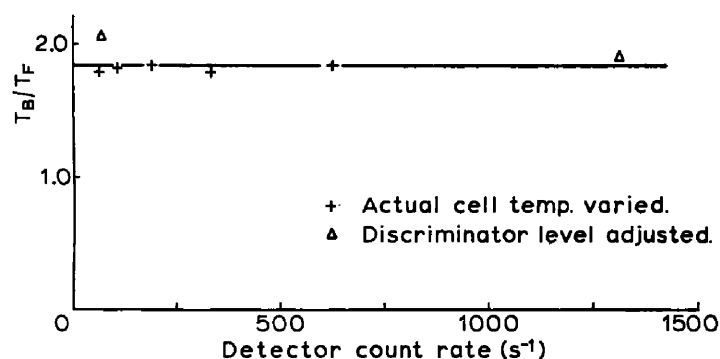


Fig. 7. Ratio of apparent beam temperature (T_B) to cell temperature (T_F) as a function of detector count rate (for varying cell temperature and discriminator level).

tions. Each data point represents the average of four measurements and the error range is shown, corresponding to an uncertainty of $\pm 25 \mu\text{s}$ (or $\pm 25 \text{ K}$).

Changing V_I and I_e causes a change in the number of ions counted, and it was found that an apparent correlation existed between the total count rate and the measured beam temperature, T_B . This is illustrated in Fig. 6, which is a normalized curve obtained from the total number of detected ions at different electron-emission currents and ion-extraction voltages, as a function of T_B/T_F . It is evident that to a first approximation such a correlation does exist. The number of detected ions can, however, be increased in several different ways. These are (a) by increasing the number of neutral particles entering the ionizer while keeping all operating conditions constant, (b) by increasing the gain of the electron multiplier, or (c) by changing the electron-emission current and ion-extraction voltages as already demonstrated. It is important to determine how these three factors independently affect the correlation shown in Fig. 6, and the results presented in Fig. 7 show that while the count rate is indeed increased by increasing both the number of neutral particles and the multiplier gain, neither of these affects T_B/T_F . It may therefore be concluded that the important parameter is not the absolute count rate, but the probability of producing a detected ion from a given number of neutrals, which is determined by the mass-spectrometer parameters V_I and I_e .

The results for a polymeric vapour, As_4 , show similar trends, with an additional factor introduced by fragmentation. Figure 8 shows the Maxwell-Boltzmann distributions fitted by the measured data for the parent ion As_4^+ , and also for the fragment ions As_2^+ and As^+ , together with a theoretical distribution corresponding to the actual cell temperature (558 K). Since there is only one parent molecule (As_4) and the spectra have been corrected for ion flight times, all of the normalized distributions should be identical. It is quite evident, however, that this is not the case, the measured beam temperature increasing with decreasing fragment mass, with T_B always greater than T_F . The TOF spectra were affected by the mass-spectrometer operating parameters in exactly the same way as those

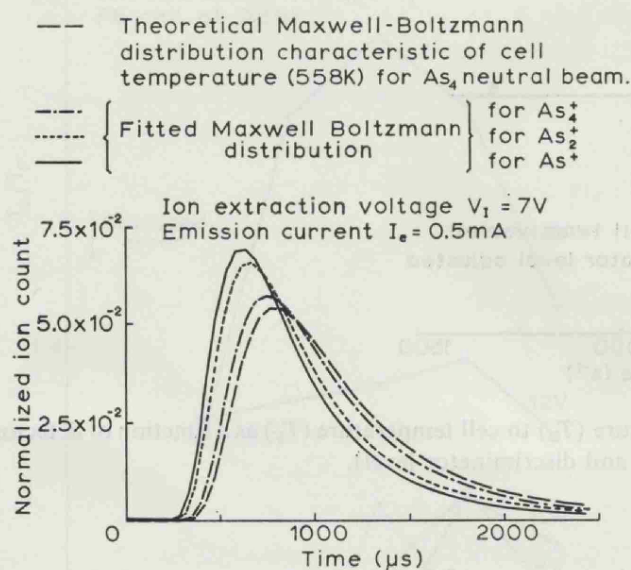


Fig. 8. Time-of-flight spectra for arsenic ions from an As_4 neutral molecule beam.

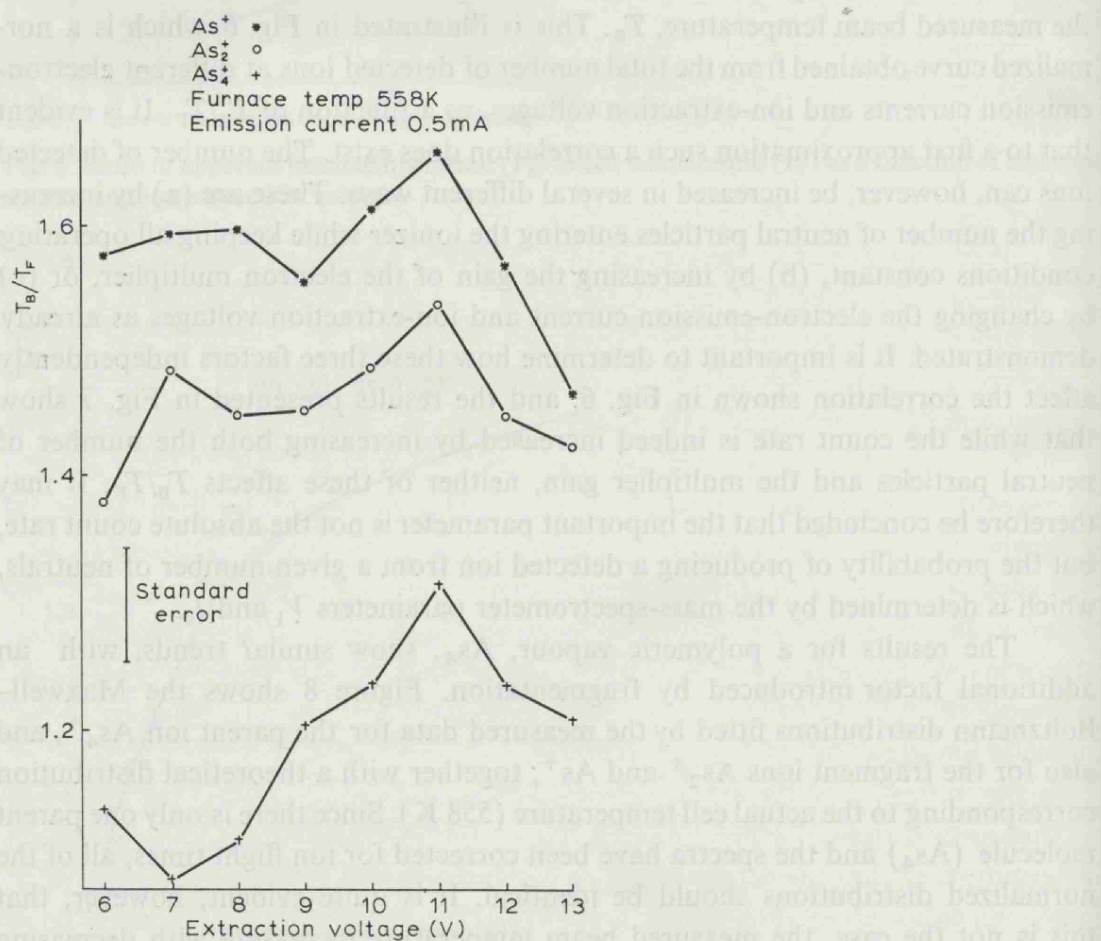


Fig. 9. Ratio of apparent beam temperature (T_B) to cell temperature (T_F) as a function of extraction voltage for various fragment ions from As_4 .

for lead. An example is shown in Fig. 9 which shows the normalized beam temperatures of As^+ , As_2^+ and As_4^+ as a function of ion-extraction voltage.

For all of the above measurements the ionizer entrance aperture was unrestricted, but it was found that by confining the neutral beam to the central region of the ionizer with a small aperture, the apparent beam temperature was considerably increased, all other parameters remaining constant. In addition, these TOF experiments have been repeated using the shutter-function deconvolution technique, and exactly analogous results obtained.

DISCUSSION

Although the influence of the detector on the measurement of TOF spectra has not previously been systematically investigated, several authors have made reference to problems encountered when using mass spectrometers. The most comprehensive account is given by Siekhaus et al. [5], who defined a so-called detector bias function for the mass spectrometer as the functional dependence of ion extraction and transmission probability on the velocity of the neutral molecule from which the ion was created. This was shown to depend on the ion-extraction voltage and the position of the neutral beam within the ionizer. These authors were concerned with measurement of the velocity distribution of molecules from a multichannel array, and their experiments did not involve changing the source temperature, but the velocity distribution from such an array contains a higher proportion of faster molecules than that from a conventional Knudsen source. They were thus able to show that to infer beam-intensity changes directly from the mass-spectrometer output signals where beam-temperature changes were also occurring required a knowledge of the detector bias function. It should therefore have been a simple matter to extend these considerations to the direct measurement of beam temperatures, from which gas-solid energy-exchange parameters are usually deduced, but their results seem largely to have been ignored in this field.

More recently Beijerinck et al. [4] have noted that with electron-emission currents > 1 mA, the measured velocity distribution from a Knudsen cell became distorted, and was no longer Maxwellian. Again, they only used room-temperature sources, and claimed that at lower emission currents they measured an exact fit to the Maxwell-Boltzmann distribution expected from a room-temperature source. Although they used an elaborate procedure for evaluating time-zero, there is nevertheless some doubt that its absolute accuracy is sufficient for this claim to be made in respect of the source temperature. The form of the distribution is not in question. Finally, Vasile et al. [11] have pointed out that it is not possible to determine the parent neutral mass of complex species by a time-of-flight measurement which assumes that the measured distribution is truly Maxwellian corresponding to the source temperature. However, these authors simply measured a phase delay and assumed the error was caused by non-ideal effusion.

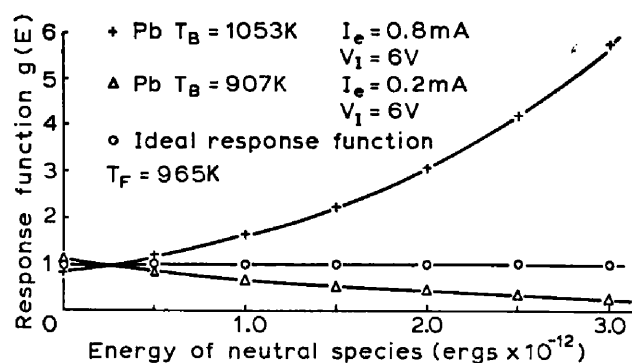


Fig. 10. Mass-spectrometer response functions.

The measurements reported here quite clearly demonstrate that the mass spectrometer is not acting as an ideal density-detector, and although the precise reasons for the observed behaviour are not evident, certain conclusions can be drawn at this stage. The most important is that the measured distribution, while not being characteristic of the correct cell temperature, is still a true Maxwell-Boltzmann distribution. It is therefore possible to define a general detector-response function $g(E, I_e, V_1)$ such that for an input function $f(E, T_F)$, the output function is $f(E, T_B)$:

$$\text{i.e. } f(E, T_B) = f(E, T_F) \times g(E, I_e, V_1) \quad (12)$$

where E is the neutral molecule energy and the other symbols are as previously defined. The parameter $g(E)$ can therefore be generated from the measured and theoretical spectra, and is of the form:

$$g(E) = \gamma \exp(\delta E) \quad (13)$$

where γ and δ are interrelated functions of only the mass-spectrometer parameters I_e and V_1 . Figure 10 shows calculated values of $g(E)$ as a function of E for $T_B > T_F$, $T_B < T_F$, and also the theoretical line for the ideal case where $T_B = T_F$.

It is evident, therefore, that the important parameter which determines the response of the detector is the energy-dependence of the probability of producing a detected ion from a given number of neutral molecules in the ionizer. It seems most likely that it is the ion-extraction process which is being affected by adjusting the mass-spectrometer operating parameters, since the actual ion-formation process is less likely to be energy-dependent (beyond that expected for the ideal density-detector mode of operation). Thus $g(E)$ is not an absolute function, but will depend critically on the instrument used, and will become more complex when additional instrument adjustments such as focussing electrodes are introduced.

It is quite evident that any attempts to use TOF techniques to determine the mean kinetic energy of neutral particles passing through the ionizer may be subject to considerable instrument error, and calibration using neutral molecules of known kinetic energy traversing the ionizer in precisely the same way as those

of unknown kinetic energy is an essential prerequisite. This geometric restriction makes the determination of gas-solid energy-exchange processes by TOF methods extremely difficult, because of the problem of ensuring that direct and scattered beams pass through the ionizer in the same way.

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ABSTRACT

Some aspects of the interaction of gas-atoms and solid-surfaces are presented. By using simple mathematical models, an intuitive understanding of the interaction between atoms and surfaces has been achieved. By a logical extension of such techniques, it is shown how a general theory for the desorption of atoms from surfaces may be formulated. Potential parameters for the gas-surface interaction are deduced for a number of experimental systems using the published data for the surface residence times of adsorbed atoms.

The growth of thin semiconducting films by Molecular Beam Epitaxy is described and the results of kinetic studies for the interaction of Ga and As₄ beams with a GaAs (100) surface are discussed. By adopting some of the previously developed atomistic concepts, a microscopic model is proposed which explains some of the fundamental aspects of the growth mechanism employed by this method.

As part of the kinetic study of Molecular Beam Epitaxy, the time-of-flight technique for measuring the velocity distribution of a beam was used. This method has been studied experimentally and detailed results are presented for As₄ and Pb neutral beams. It is shown that when a quadrupole mass spectrometer with a cross beam ionizer is employed as a detector, serious errors arise from inherent time delays, which are observed to be strong functions of several operating parameters. The consequence of this instrument malfunction is discussed with particular reference to the measurement of energy accommodation coefficients.