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THE ADSORPTION OF THE INERT GASES ON SODIUM CHLORIDE AND POTASSIUM CHLORIDE

by

WILLIAM ALAN HOUSE, B.Sc.

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology

October 1975

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DECLARATION OF ORIGINALITY

The work in this thesis is the original work of the author throughout the text, except where otherwise acknowledged, and has not been presented previously, wholly or in part, for the award of any degree in any University.

October 1975

W.A.H.
SUMMARY

The adsorption of the inert gases on the (100) face of sodium chloride and potassium chloride is studied to determine the probable state of the adsorbed atom. This involved a detailed analysis of the interatomic forces that are important in physical adsorption and limiting potential models are suggested for the determination of the gas atom-solid potential energy field. Expressions for the determination of the electrostatic interaction of the adsorbed atom with the surface are also presented.

The affect of allowing the ideal (100) surface to relax to its equilibrium conformation is found to be appreciable for the interaction of argon and krypton with (100) sodium chloride but less important for their interaction with (100) potassium chloride. The changes in adsorption properties occurring because of surface relaxation are investigated using the hindered translation model.

The argon-sodium chloride system is further investigated by using the gas-solid virial analysis. This is made possible by developing expressions for the electrostatic field above the relaxed (100) surface and a double Fourier expansion of the non-electrostatic potential energy field. The results indicate substantial perturbation of the ideal two-dimensional virial coefficient at temperatures < 120K. The third body (surface) interactions at the interface are considered together with the applicability of the two-dimensional approximation for the adsorbate self-interaction. The approach is also used to calculate the Henry's law constant and isosteric enthalpy for the argon-sodium chloride system. The results are found to be in agreement with those obtained using the hindered translation model.
Samples of good quality sodium chloride crystals are prepared and the krypton and argon adsorption isotherms at the liquid nitrogen temperature are measured. The isotherms are analysed by using a numerical algorithm, ADSEFF, that is developed for the computation of patchwise site energy distribution functions from adsorption isotherm data by using either a mobile adsorption model or a localized one. The low pressure region of the argon isotherm at 76.1K is analysed by using the two-dimensional virial equation.
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CHAPTER 1

GENERAL INTRODUCTION

The measurement of the equilibrium behaviour of gas atoms physically adsorbed on solid surfaces is a useful way of developing a knowledge of some of the surface properties. At the same time it offers an opportunity to study the behaviour of gas atoms held in the potential field of the solid.

Previous studies have been concerned with a whole range of combinations of gas-solid systems. The most useful studies, in terms of the understanding of the process of physical adsorption, have been those of inert gas atoms adsorbed on inert gas crystals and inert gas atoms adsorbed on graphitized carbon blacks. In these cases the surfaces are highly homogeneous so that a theoretical description of adsorption is possible. Even so, the complexity of the interfacial region has meant that a large number of problems remain unsolved. Adsorption on ionic solids is less advanced, although multilayer adsorption theories, such as the BET, are commonly used to determine surface areas. In most cases the models used are crude and recognized to be unrealistic. Monolayer adsorption theory is more advanced, particularly in taking account of surface inhomogeneities. It is in the region of the adsorption isotherm where multilayer effects are unimportant that most information can be obtained about the surface structure. The present work is solely concerned with monolayer adsorption.

With the possibility of preparing reasonably homogeneous samples of the alkali-halide crystals, scope exists for investigating the adsorbate state. If some understanding of the more
ideal of systems is obtained, this can be profitably used when analysing more heterogeneous samples. In the present work the inert gas – sodium chloride/potassium chloride systems are chosen because:

(i) The inert gas atoms are monatomic and of simple electronic structure, which means that rotational and intramolecular vibrational changes of molecules on adsorption do not need to be taken into account.

(ii) The inert gas atoms self-interaction potential energy functions are more advanced than for the other possible gaseous adsorbates.

(iii) The inert gases have been commonly used as adsorbates in the determination of experimental adsorption isotherms.

(iv) Sodium chloride and potassium chloride are highly ionic crystals, consequently the electrostatic field above the surface can be calculated with some certainty.

(v) These salts are the most widely studied of the ionic crystals, and as a result, a great deal of information is available about them.

(vi) These crystals are amongst the few for which studies of the surface distortion have been made.

In the limit of very low concentrations of adsorbed atoms on the surface, the single atom-surface interaction characterizes the adsorption isotherm. This is a complex interaction that can only be calculated by making certain approximations. In this work the gas-surface potential is obtained by a summation of the individual gas-ion pair interactions. This in itself necessitates a careful examination of the interatomic potential function for both the inert gas self-interaction and the ion self-interactions within
the solid. This whole subject is discussed in Chapter 2, resulting in a number of models being suggested for the gas-ion potential energy functions. Two derived gas-surface potential energy fields are presented in Chapter 3 and analysed using a model that allows the atom varying translational degrees of freedom, ranging from completely free two-dimensional motion to localized vibrational motion.

At slightly higher adsorbate concentrations, the inert gas lateral interactions begin to become important. A convenient way to account for this is by examining the second two-dimensional virial coefficient and its perturbation by the presence of the solid substrate. Usually this is done by assuming that the gas-surface field is constant over the whole surface and hence the perturbation by the solid is zero. In Chapter 4 the second two-dimensional virial coefficient, for argon on sodium chloride, is computed taking account of the periodic nature of the external potential field.

The experimental determination of adsorption isotherms of gases on solids is now well established. The main problem in the present treatment is preparing samples of sufficient quality for a comparison of results with theoretical findings. This means that certain criteria are required to assess the homogeneity of the samples. This incorporated a separate study of the determination of adsorption energy distribution functions from isotherm data (Chapter 5). Since the low pressure region of the isotherm is important in this work, particular care is required in the adsorption measurements and their subsequent use in the calculation of the adsorption isotherm. This is discussed in Chapter 6 together with the methods used to prepare the relatively homogeneous samples. The final
analysis of results in Chapter 7 is concerned with the determination of the heterogeneity of crystals prepared by different methods and subsequent analysis of the low pressure region of the isotherms. The results are restricted to an analysis of adsorption data obtained at liquid nitrogen temperatures.
CHAPTER 2

INTERATOMIC POTENTIALS

2.1 INTRODUCTION

The total potential energy of two atoms or ions interacting through electrostatic force laws is given by:

$$\phi(r_{12}) = \frac{1}{2} \sum_{i \neq j=1}^{n} \frac{Z_1^2 e^2}{r_{ij}} - \sum_{i=1}^{n} \left( \frac{Z_1 e^2}{r_{i1}} + \frac{Z_2 e^2}{r_{i2}} \right) + \frac{Z_1 Z_2 e^2}{r_{12}}$$

(2.1)

where: $Z_1 e$ and $Z_2 e$ are the atom or ion nuclear charges, the subscripts referring to the atom or ion type.

$r_{ij}$ is the separation distance between $i$th and $j$th electrons.

$n$ is the total number of electrons.

If the assumption is made that the electronic and nuclear components of the wavefunction describing this system are separable (Born-Oppenheimer approximation (see Atkins 1970)), then when (2.1) is used in the Schrödinger equation, the resulting eigenvalue equation formally gives the ground state energies. A comparison with the total energy of the two isolated atoms or ions will give the interaction energy, $U(r_{12})$. Apart from two hydrogen atoms or two ground state helium atoms (Kestner, 1966), this many-body system is too complex for an accurate solution to be obtained. The interaction energy is a small percentage of the two atoms' total energy and so the difference in energy required is very sensitive to any approximations that are made. This is particularly important when using the self-consistent field method of Hartree (1955). He replaced the many-body interaction between one electron and all the
rest of the atomic electrons by that which would result from a
space-averaged charge distribution summed over those electrons and
assumed to be spherically symmetrical. The Schrödinger equation
for the motion of the electron in this average potential may then
be solved. The three interrelated variables in the Hartree pro-
cedure, namely the wavefunction of an n-electron atom, the central
potential and the charge density, are connected by the Schrödinger
equation and the laws of electrostatics. The basic problem is to
arrive at a charge distribution and average potential that are
self-consistent. This implies that the wavefunction is originally
known so the average potential may be calculated. In fact an
initial approximation is made for the atomic wavefunction by a
suitable combination of electron functions. Using this potential,
the equation for a particular electron is solved and the wavefunction
so calculated is adopted to refine the potential, which another
electron experiences in the atom. This procedure is repeated for
each of the electrons until a self-consistent solution is obtained.

In Hartree's original method there was no correlation between
the motion of individual electrons; each moved in an averaged field
and the simple product wavefunction implied a statistical independ-
ence between their motion. The Hartree-Fock method, (Hartree 1955),
is based on the use of antisymmetric wavefunctions. This introduces
a correlation between electrons with like "spin", so there is zero
probability of two electrons having the same spin and occupying the
same point in space, but no correlation occurs between electrons
with opposite spin. In spite of this limitation, Hartree-Fock's
method can give absolute energies with errors of less than 1%. The
remaining problem is to solve (2.1) to an accuracy capable of giv-
ing reliable interaction energies; at the moment this is not possible.
However this does not mean that a theoretical approach is not useful. Approximate methods such as second-order perturbation theory and variation theory have yielded much information regarding the form of the potential energy curve at large interatomic separations.

Short range forces are less well defined. Their physical origin is clearly the repulsion between closed electron shells, and at closer distances, internuclear repulsions. They appear in a first-order perturbation energy calculation. However, because of the overlap effects, enormous complications are introduced which necessitate the use of correctly symmetrized wavefunctions for the electrons. One method to overcome this is to use the Thomas-Fermi-Dirac statistical model of the atom, (see Torrens 1972), discussed in §2.3.1. Experimental methods of investigating this region of the potential energy function are also available.

The approximations that generally yield results for either the long-range interaction or the short-range interaction, fail in the intermediate region of the potential well minimum. Hence apart from increasing the reliability and interpretation of molecular beam scattering data in this energy region, the only way to study the potential well is by using the macroscopic dilute gas properties that are dependent on separable two or more body forces, i.e. bulk phase gas virial coefficients, viscosity, thermal conductivity, self-diffusion coefficients and isotropic thermal-diffusion factors.

In the case of the interaction between gas atoms and the surface, the problem is more complex. Second order perturbation theory could be used to determine the long range interaction (Sinanoglu and Pitzer 1960), or alternatively the Gordon-Kim density functional method (Freeman, 1975a) could be employed but both methods require
an accurate knowledge of the electronic structure of the solid surface. The density functional method also requires accurate solid band wavefunctions. These methods are attractive because they are realistic in representing the solid as an entirety, rather than trying to deal with the uncertainties associated with examining the individual gas-ion interactions. However, they are impractical at the present time due to inadequacies in describing the solid surface in terms of accurate wavefunctions.

The best approach is to determine the potential function for the individual ion-inert gas interaction, through the use of combination rules. These allow the specification of the gas-ion potential from the individual gas self-interaction and the ion self-interaction potentials. The gas-solid potential field may then be obtained by using the pairwise additive approximation. This allows the potential field to be determined by summing the single interactions of the gas atom with the ions within the solid. This is a deficiency in the present treatment since it is realised that the pairwise additive approximation may be a poor one. However, it is a method of obtaining the potential field which may be subsequently used to compare derived theoretical and experimental properties associated with the adsorbate. In this manner it is possible to use the gas-ion potential as a variable in order to change the potential energy field.

2.2 LONG-RANGE FORCES

2.2.1 Perturbation Calculation

The fundamentals of this method have been reviewed by a number of researchers, the most comprehensive treatment being given by Margenau (1939). The details of this method will not be reproduced here, but it is worthwhile to consider the steps that lead to a
useful result, and also the limitations inherent in the models that are still commonly used.

The perturbation being considered is an interaction between two electric dipole moments, one on atom 'a', \( \mathbf{d}(a) \) and the other on atom 'b', \( \mathbf{d}(b) \). If the atoms are separated by a vector, \( \mathbf{r} \), the interaction Hamiltonian may be written as:

\[
\hat{H}(1) = \frac{1}{r^3} \left[ \mathbf{d}(a) \mathbf{d}(b) - 3 \mathbf{d}(a) \left( \frac{\mathbf{r} \cdot \mathbf{r}}{r^2} \right) \mathbf{d}(b) \right]
\]

(2.2)

and the unperturbed Hamiltonian as the sum of the Hamiltonians for the atoms infinitely separated and the wavefunction as simple product wavefunctions of the isolated atoms:

\[
\psi_{mn}^0 = \psi_m^0(a) \psi_n^0(b)
\]

(2.3)

where \( m \) and \( n \) label the quantum states.

The use of (2.2) and (2.3) restrict the application of this method to systems where the atoms are not overlapping. The reason for this is that the multipole expansion of the type (2.2) is not valid for overlapping dipoles, and the unsymmetrized wavefunctions (2.3), \( \psi_{mn}^0 \), are not accurate when the electron clouds approach closely or overlap.

Applying perturbation theory, (Atkins 1970), the second order perturbation energy becomes:

\[
E^{(2)} = -3e \sum_{K K'} \left( \sum_{K} \frac{f(K) f(K')}{(E_K + E_{K'} - E_0 - E_0) (E_K - E_0)} \right)
\]

(2.4)

where \( E_0 \) is the ground state energy, \( E_K \) the energy of the \( K \)th electronic state and \( f(K) \) the oscillator strength given by:

\[
f(K) = \frac{2}{3} \frac{E_K - E_0}{e^2 a_0^2} | \langle 0 | \sum_{i} \mathbf{r}_i | K \rangle |^2
\]

(2.5)
where the Dirac, Ket and Bra notation is used (Atkins 1970).

For convenience the electronic states of the atoms 'a' and 'b' are labelled K and K'. The sums in (2.4) are over all states excepting the ground state. (This omission, which is a common result in perturbation theory, e.g. Atkins 1970, is indicated by the accent over the summation sign).

By substituting (2.5) into (2.4) and replacing the sums in (2.4) by \( \Delta \) and \( \Delta' \), the effective energy differences, (Unsold's closure approximation; Atkins 1970), \( E^{(2)} \) becomes:

\[
E^{(2)} = -\frac{2e^4}{3r^6} \frac{\langle \sum_{i=1}^{4} |r_i^2| \rangle - \langle \sum_{i=1}^{4} |r_i' \rangle^2 \rangle}{\Delta + \Delta'}
\]  

(2.6)

This may be further simplified by using the expression for the atomic polarizability:

\[
a = \frac{2e^2}{3} \sum_{K} \frac{\langle \sum_{i=1}^{4} |r_i^2| \rangle}{(E_K - E_0)}
\]

(2.7)

Using the closure approximation, (2.7) may be substituted into (2.6) to give the major term contributing to the dispersion energy of interaction:

\[
E^{(2)} = -\frac{3}{2} \frac{\Delta \Delta'}{r^6} \frac{\alpha_a \alpha_b}{\Delta + \Delta'}
\]

(2.8)

### 2.2.2 The Kirkwood-Müller Equation

The "effective energies" \( \Delta \) and \( \Delta' \) may be replaced in (2.8) by using (2.7). This assumes that the "effective energies" remain unchanged as the atoms approach each other.
The correlation term may be expanded:

\[ E(2) = -\frac{e^2}{r^6} \sum \frac{a_a a_b}{\langle \sum_i \mathbf{r}_i \rangle^2 + \langle \sum_i \mathbf{r}_i' \rangle^2} \]  

(2.9)

The correlation term may be expanded:

\[ \langle \sum_i \mathbf{r}_i \rangle^2 = \sum_i \langle \mathbf{r}_i^2 \rangle + \sum_{i \neq j} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle \]  

(2.10)

\[ = -\frac{6mc^2 \chi_{\text{dia}}}{e^2} + \sum_{i \neq j} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle \]  

(2.11)

where

\[ \chi_{\text{dia}} = \text{diamagnetic susceptibility of the atom} \]

\[ m = \text{rest mass of an electron} \]

\[ c = \text{speed of light} \]

If the second negative correlation term in (2.11) is neglected, 

\[ E(2) \] reduces to the Kirkwood-Müller [KM] equation.

\[ E(2) = \frac{6mc^2}{r^6} \sum \frac{a_a a_b}{\alpha_a/\chi_a + \alpha_b/\chi_b} \]  

(2.12)

Salem (1960) has shown that the negative correlation term lowers the value of \( E(2) \), and concludes that the KM equation is the best approximation available to the dispersion energy. In fact, as will be now shown, an error of about 20% is introduced by neglecting the correlation term. This may be proved by a calculation using Slater's analytical functions of the Hartree-Fock solutions. The correct Slater determinant may be formed for the various two electron functions, and the expectation value of the operator determined in the usual manner from the normalized wavefunctions

\[ \psi_{n^2 m}(r, \theta, \phi) = N \gamma_{n^2 \alpha_0} \exp \left\{ \frac{(z - \sigma)r}{\gamma_{n^2 \alpha_0}} \right\} \chi_{n, m}(\theta, \phi) \]  

(2.13)
where
\[ n = \text{number of electrons}. \]
For \( n = 1,2,3; n^* = n; n = 4,5,6; \]
\( n^* = 3.7, 4.0, 4.2. \)

\( z = \text{atomic number}. \)

\( \sigma = \text{effective shielding constants given by Slater.} \)

\( Y_{l,m}(\theta, \phi) \) are the spherical harmonics for the single

wavefunctions written in terms of polar coordinates \( \theta \) and

\( \phi, \) the co-latitude and azimuth angles respectively.

For neon the following normalized wavefunctions are obtained:

\[ \psi_{100} = \frac{(9.7)^{3/2}}{a_0^{3/2} \pi} \exp(-9.7r/a_0) \quad (2.14) \]

\[ \psi_{200} = \frac{(5.85)^{5/2}}{a_0^{5/2} r^{3} (5)^{1/2} 2\pi} r \exp(-5.85r/2a_0) \quad (2.15) \]

\[ \psi_{210} = \frac{\sqrt{3}}{2\pi a_0^{5/2}} \frac{(5.85)^{5/2}}{r^{3} (5)^{1/2}} r \exp(-5.85r/2a_0) \cos \theta \quad (2.16) \]

\[ \langle r_1, r_2 \rangle = \int_0^\pi \int_0^{2\pi} \int_0^\infty \psi^*(1,2) r_1 r_2 \cos \theta \cos \phi \cdot \sin \theta_1 \sin \phi_1 \\
\times (r_1 r_2 \sin \theta_1 \sin \phi_2 - r_1 r_2 \sin \phi_1 \sin \phi_2, r_1 r_2 \phi(1,2)) dr_1 dr_2 \]

\[ \sin \theta_1 \sin \phi_1 dr_1 d\phi_1 d\theta_1 d\phi_2 \quad (2.17) \]

Application of these equations gave a total correlation term
of \(-1.47 \text{ au}, (1 \text{ au} = 28.0007 \times 10^{-18} \text{ cm}^2), \) which compares with

\(-1.50 \text{ au} \) obtained previously by Vinti (1932). The main difficulty
in the sum calculations is the sensitivity of the magnitude of the
correlation term to the wavefunction adopted. In the above

calculation the correlation terms for electrons with opposite spins
are zero. In the case of helium, Vinti (1932) calculated
\[ \left\langle r_i \cdot r_j \right\rangle = -0.146 \text{ au.} \]
using wavefunctions that gave the energy correct to one part in three thousand. A more accurate calculation for helium is that due to Pekeris (1959) who calculated a value of 
\[ -0.06474 \text{ au.} \]
This discrepancy illustrates the difficulty.

Salem (1960) determined the correlation term for argon, krypton and xenon by comparing the \( c_6 \) values, \( E^{(2)} = c_6/r^6 \), obtained from the Lennard-Jones equation (see §2.4), with the KM values. This gave \( \sum_{i \neq j} \left\langle r_i \cdot r_j \right\rangle \) of the expected magnitude and showed an error of \( \approx 20\% \) for all the gases. Unfortunately the Lennard-Jones \( c_6 \) values are in poor agreement with those obtained by Kingston (1964) from experimental oscillator strengths. A similar comparison using the \( c_6 \) values of Kingston (1964) leads to an error of \( 58\% \) for neon. This is too large to be solely attributed to the neglect of the correlation term. Since the Kingston values are in agreement with the Barker-Leonard (1964) values and both are quoted to an accuracy of a few per cent, the closure approximation used in the derivation of (2.12) seems to have a more significant effect.

2.2.3 The Variation Calculation

This method allows a trial wavefunction, in practice an unperturbed function multiplied by a perturbing factor, to be used to minimize

\[ \Delta E = -\int \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} \, dr / \int \psi_{\text{trial}}^* \psi_{\text{trial}} \, dr \]  

(2.18)

where \( \hat{H} \) is the Hamiltonian operator. This is accomplished by adjustment of variables in \( \psi_{\text{trial}} \). The method was first applied by Hassé (1930) to the calculation of dispersion forces. This calculation gave:
\[ c_6 = \frac{12me^4}{h^2} \sum_{ij} \frac{u_i^2 u_j^2}{u_i + u_j} \]  
\[ \alpha = \frac{4me^2}{h^2} \sum_i u_i^2 \]  
where \[ \langle 0 | r_i^2 | 0 \rangle = u_i \]  
and \[ \langle 0 | r_j^2 | 0 \rangle = u_j \]

As with perturbation theory, the problem becomes one of accurately specifying the symmetrized \( \Psi_0 \) functions. In order to evaluate (2.19) the approximation is made:

\[ u_i = u \quad \text{for } i = 1, n_a \]
\[ u_j = u' \quad \text{for } j = 1, n_b \]

so that
\[ \alpha = \frac{4me^2}{h^2} n_a u_a^2 \]

Substituting (2.23) into (2.19) yields:

\[ c_6 = -\frac{3en_a n_b}{2m} \left( \frac{\alpha_a^1}{n_a} + \frac{\alpha_b^1}{n_b} \right) \]

This is called the Slater-Kirkwood, (SK), equation first presented by Slater and Kirkwood (1931).

Condition (2.22) limits the usefulness of the SK treatment since there is uncertainty about the value of \( n_a \) and \( n_b \). In the past \( n_a \) and \( n_b \) have been equated to the number of outer shell electrons. This generally leads to a lower limit to the \( c_6 \) value.

However, Wilson (1965) points out that the outer \( p \) electrons in the inert gases heavier than neon, are more effectively shielded than the outer \( s \) electrons. Hence for argon, krypton and xenon an \( n \) value...
of 6 ought to be more realistic. Wilson determined the n values from a comparison of (2.24) with the Kingston (1964) and Barker and Leonard (1964) C_6 values. Table 2.1 presents the results of this analysis.

**TABLE 2.1 EFFECTIVE ELECTRON NUMBERS FOR THE SK EQUATION**

<table>
<thead>
<tr>
<th>gas electron number</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>n(K)</td>
<td>1.42</td>
<td>3.76</td>
<td>5.60</td>
<td>6.50</td>
<td>6.35</td>
</tr>
<tr>
<td>n(BL)</td>
<td>1.49</td>
<td>3.89</td>
<td>5.82</td>
<td>6.49</td>
<td>6.70</td>
</tr>
</tbody>
</table>

If these n values are used in (2.24) for the unlike inert gas C_6 determinations, good agreement with the mixed C_6 constants of Kingston (1964) are obtained. This suggests that the functional form of (2.24) is correct.

2.3 SHORT RANGE FORCES

2.3.1 The Thomas-Fermi-Dirac Statistical Model

The short range repulsive forces may be resolved using first order perturbation theory with correctly symmetrized wavefunctions for each of the atoms. In practice a solution to the problem is too complex. For this reason the Thomas-Fermi-Dirac (TFD) model has been used to predict short range repulsion energies. The method has given good comparison with high energy atomic scattering data (§2.3.2) and information about the previously unknown short range
region of the potential energy function.

The method is based on the Fermi-Dirac theory of a free electron gas. This is applicable when the potential energy changes are small in a volume localizing many electrons. The electrons are then considered to be elements of a degenerate electron "gas". Exchange energy effects can be introduced into the treatment. The resulting TFD electron density exhibits a sharp cut off known as the TFD radius. This means there is no interaction between the atoms at a distance greater than the sum of the two atoms TFD radii. The model has been reviewed in detail by Torren (1972) and so only the basic results will be discussed here.

The analysis indicates that the short range interaction energy may be expressed in the Born-Mayer, [BM], form:

\[
U^{\text{rep}} = c_1 \exp(-c_2 r) \tag{2.25}
\]

The majority of the work has been done for the inert gases. In particular Abrahamson, Hatcher and Vineyard (1961) and Abrahamson (1963, 1964, 1969) have tabulated values of \(c_1\) and \(c_2\) for a number of systems. Gaydaenko and Nikulin (1970) have repeated the calculation using Hartree-Fock electron densities rather than the TFD distributions used by Abrahamson. They show that the relationship (2.25) is still obeyed but Abrahamson's results overestimate \(U^{\text{rep}}\) by a factor of 1.5 - 2. This is not surprising in view of the findings of Wedepohl (1967) who examined the sensitivity of \(U^{\text{rep}}\) to the details of the electron distribution.

The limitations of the method become obvious when results of accurate quantum mechanical calculations are produced. Slater (1928), Rosen (1950), Griffing and Wehner (1955) and Phillipson (1962) have obtained results for helium repulsion which include
terms dealing with electron correlation. The most up-to-date results of Phillipson (1962) are not in agreement with any of the statistical models and hence cast doubt on their validity. However the TFD model is more accurate for larger atoms since the individual nature of each electron is less marked, and the concept of atoms as single charge distributions becomes more realistic.

2.3.2 High Energy Atomic Scattering

The scattering of one atom by another is possibly one of the most direct experimental means of obtaining information about the interaction potential. The discussion here is restricted to inert gas atom collisions. Although these are the most widely studied, methods are still being developed to obtain more reliable potential energy functions.

The procedure consists of producing a well defined collimated monoenergetic beam of atoms or ions and passing this through a scattering chamber containing target atoms at room temperature. The energy of the beam must be below 3-4 keV or else inelastic scattering will result i.e. ionization of the atoms will occur. The value of the beam energy will determine what region of the potential energy function the subsequent analysis will apply. In high energy atomic scattering this is the repulsion region of the potential energy curve. The total cross-section, $S$, may be obtained by measuring the difference in beam intensity reaching a detector placed directly behind the scattering chamber with and without the gas of target atoms present. Hence $S$ is the total number of particles scattered into all solid angles per unit incident intensity. A more useful quantity for determining interatomic potentials directly is the differential scattering cross-section $\sigma(\phi)$. This is defined as the
fraction of the incident intensity scattered into unit solid angle about the direction of the incident beam. The important parameter that provides the link between the scattering cross-sections and theoretical single collision equations is the impact parameter, $s$. This is the length of the perpendicular between the target atom and incident trajectory. In terms of the differential scattering cross-section and planar scattering angle $\phi$, this is expressed (Torrens 1972):

$$s^2(\phi) = 2\int_0^{\pi} \sigma(\phi) \sin \phi d\phi$$  \hspace{1cm} (2.26)

It is possible to express the impact parameter in terms of the interatomic potential. The total collision cross-section may also be expressed in terms of the differential cross-section

$$S = 2\pi \int_0^{\pi} \sigma(\phi) \sin \phi d\phi$$  \hspace{1cm} (2.27)

Most of the earlier work in this field measured $S$, and used simple analytical forms of the potential function containing variable parameters. These were used to give the best least-squares fit to theoretical $S$ data generated from the generalized potential functions. Amdur and co-workers (1954, 1955a, 1955b, 1956, 1961, 1966) have made extensive investigations for the inert gas interactions. Their results, for argon, are compared in fig. 2.1 to values derived by other methods.

At the moment the reliability of the results depends upon the beam detector geometry and the beam geometry. The beam must have finite width to provide sufficient intensity at the detector. Thus even if the beam is perfectly collimated some particles may be scattered at the edges and exit holes of the target chamber. If the beam energy falls to values such that the interatomic potential
Fig. 2.1 Short-range interatomic potentials for the argon self-interaction

Key:
1. 20-6 bireciprocal potential
2. "exp6" from TP
3. "exp6" from SP
4. this work; Kingston $C_6$ with $c_1$ and $c_2$ optimized from bulk second virial coefficients used by TP
5. "exp6" Mason and Rice (1954)

---
atomic scattering data
---
Dymond and Alder (1969)
minimum becomes important in the two body interactions, the potential curve cannot be determined. This is because for a given deflection, \( \phi \), the impact parameter is not determined. This problem may be avoided by increasing the beam energy so that only the repulsive part of the potential influences the scattering.

Useful information can also be obtained in the range of lower beam energies where dispersion forces predominate the gas interactions. The method has not been as successful as the high energy beam work (Pauly and Toennies 1965). However, Rothe and Neynaber (1965) have obtained good correspondence of their \( C_6 \) terms with those of Kingston (1964), Barker and Leonard (1964).

2.4 SEMI-EMPIRICAL EQUATIONS

Many generalized semi-empirical analytical functions have been suggested, the form of which can be justified from the theoretical considerations.

It is the purpose here to review some of these functions and, guided by the previous discussion, obtain a workable form for the inert gas self-interaction potential function.

The simpler models, i.e. the rigid elastic sphere, rigid elastic parallel cube, soft sphere, square well, triangular well, trapezoidal well and Sutherland, although having applications in situations when the more sophisticated functions are too complex to handle, are not considered here.

The simplest two-parameter function is the bireciprocal potential or Mie (1903) potential:

\[
U(r) = \frac{K_n}{r^n} - \frac{K_m}{r^m} \quad \text{with } n > m > 3 \quad (2.28)
\]

The most common form of (2.28) is the Lennard-Jones 6-12 potential (LJ):
\[ U(r) = -2\varepsilon \left( \frac{r_m}{r} \right)^6 + \varepsilon \left( \frac{r_m}{r} \right)^{12} \]

or

\[ U(r) = 4\varepsilon \left[ -\left( \frac{\sigma}{r} \right)^6 + \left( \frac{\sigma}{r} \right)^{12} \right] \]

where \( r_m = 2^{1/6} \sigma \) and \( \sigma \) is the hard sphere diameter. This function gives:

\[ U'(r) = 0 \quad \text{at} \quad r = r_m \quad \text{and} \quad U(r) = \varepsilon \]

and

\[ U(r) = 0 \quad \text{at} \quad r = \sigma \]

The theoretical treatments illustrated in fig. 2.1 indicate that the best bireciprocal potential ("20-6") determined by TP has too large a gradient for \( r < 2.6\sigma \).

To give more flexibility to the LJ function, a third parameter may be introduced which effectively takes account of the rigid central core of the atoms. This leads to the spherical-rigid-core Kihara model:

\[ U(r) = \varepsilon \left[ \frac{r_m}{r - d} \right]^{12} - 2\left( \frac{r_m}{r - d} \right)^6 \]

(2.30)

\[ U(r) = \infty \quad \text{for} \quad r \leq d \]

where \( \sigma = 2^{-1/6} r_m + d \)

Another three parameter potential is the modified Buckingham potential function or "exp6", (Mason and Vanderslice 1958), derived from the Buckingham (1937) potential function. It is superior to (2.28) and (2.30) because of the BM form of the repulsive region

\[ U(r) = \frac{\varepsilon}{1 - \frac{6}{6/\alpha}} \left\{ \frac{6}{\alpha} \exp[\alpha(1 - r/r_m)] - (r_m/r)^6 \right\} \]

(2.31a)

for \( r > r_{\text{max}} \)

\[ U(r) = \infty \quad \text{at} \quad r \leq r_{\text{max}} \]

(2.31b)

where \( \varepsilon \) and \( r_m \) have their usual meaning. The dimensionless
third parameter, \( \alpha \), is a measure of the steepness of the repulsive curve. Equation (2.31a) may be subdivided:

\[
U^{\text{rep}} = \frac{6\epsilon}{\alpha - 6} \exp(\alpha) \exp(-\alpha r/r_m)
\]

(2.32a)

\[
U^{\text{dis}} = \left[\epsilon/(1 - 6/\alpha)\right] (r_m/r)^6
\]

(2.32b)

where \( U^{\text{dis}} \) is the long range dispersion interaction. An examination of (2.32b) reveals that \( U^{\text{dis}} \) also depends on \( \alpha \). This means the "head" of the potential energy function is linked to the "tail", resulting in some loss of flexibility. The \( r_{\max} \) value is determined from a numerical solution of the transcendental equation:

\[
(r/r_m)^7 \exp[a(1 - r/r_m)] - 1.0 = 0
\]

(2.33)

(2.33) is obtained using the method of Lagrange multipliers. The hard sphere diameter, \( \sigma \), may be obtained from (2.31) by a numerical iterative procedure. In fact (2.31) is the reduced form of the general function:

\[
U(r) = c_1 \exp(-c_2 r) - C/r^6
\]

(2.34)

where \( c_1 \) and \( c_2 \) relate to the BM equation for \( U^{\text{rep}} \), and \( C \) is a constant determined from the long range interaction. Knowing \( c_1 \), \( c_2 \) and \( C \) the reduced parameters \( r_m \), \( r_{\max} \), \( \epsilon \), and \( \sigma \) may be obtained by a numerical procedure. The value of \( \alpha \) follows from a comparison of (2.32b) with (2.34).

Finally, the Boys and Shavitt (1956) potential energy function is a more generalized function containing as many adjustable parameters as required

\[
U(r) = \frac{4\epsilon}{(y^2 + B^2)^3} \sum_{i=0}^{\infty} C_{2i} y^{2i} \exp[A(1 - y^2)] - 1
\]

(2.35)

where \( y = r/\sigma \) and \( A, B, C_{2i} \) \((i = 0,1,2,\ldots)\) are adjustable parameters.
If \( A = 4, \ B^2 = 0.1 \) with \( C_0 = 1 \) and \( C_{2i} = 0 \) for all \( i \), then the potential reduces to a form similar to the Lennard-Jones function. A convenient form of (2.35) is obtained with \( B = 0 \) (to give the correct asymptotic \( r^{-6} \) behaviour) and for computational convenience, \( A = 4 \). Munn (1964) has shown that the constants \( C_0, C_2, C_4 \) and \( C_6 \) may be obtained by specification of three separate potential energy regions:

(i) \( U(r) > 0 \) or \( r < \sigma \)

(ii) \( r = \sigma \) to \( r = r_m \)

(iii) \( r = r_m \) to \( r = \infty \)

which correspond to the conditions:

\[
\begin{align*}
U(y) &= 50\epsilon \quad \text{for } y < 1 \\
U(r_m) &= -\epsilon \quad \left( \frac{dU(r)}{dr} \right)_{r_m} = 0 \\
\lim_{r \to \infty} (U(r) \cdot r^5) &= c_6
\end{align*}
\]

(2.36)

Although the Boys and Shavitt (1956) function is more flexible than the others, the criteria for the choice of the interaction potential function is guided by a number of points:

(i) The great difficulty determining the variable parameters in any potential function adopted.

(ii) The mathematical form of the function.

(iii) Whether the parameters can be determined for the ion-ion interaction (see §2.9).

Because of (i) and (ii) the Boys and Shavitt function is not used. Instead the "exp6" potential function is adopted here.

2.5 THE DETERMINATION OF PAIR-POTENTIAL PARAMETERS FROM BULK PHASE VIRIAL COEFFICIENT DATA

The bulk second virial coefficient is determined solely through
two-body interactions. Hence this method of determining interaction potential parameters is most useful. The analysis of the third virial coefficient is more sensitive to the choice of potential function and three-body effects have to be taken into account. It is possible to determine these three-body effects for the inert gases, and hence the method, coupled with dilute gas transport properties and atomic scattering, provides a powerful means of establishing potential energy functions.

A discussion of the derivation of the virial series for monatomic gases is given by Hill (1960). The virial coefficients correspond successively to interactions between pairs, triplet etc. of atoms so that the virial equation of state in effect reduces the many-body problem of the gas as a whole, i.e. to a series of one-body, two-body, three-body, ... terms. The grand partition function for the system of monatomic atoms permits this interpretation of the terms of the virial equation.

The series may be written in terms of a density expansion:

\[
\frac{PV}{RT} = 1 + B\rho + C\rho^2 + D\rho^3
\]  

(2.37)

where \( \tilde{V} \) is the molar volume

\( \rho = 1/\tilde{V} \)

and \( B, C, D \) are the second, third and fourth virial coefficients.

In the classical limit, the coefficients are given in terms of the configurational partition functions, \( Q_N \)

\[
B = -\frac{L}{2\tilde{V}} (Q_2 - Q_1^2)
\]  

(2.38)

\[
C = -\frac{L^2}{3\tilde{V}^2} \left[ V(Q_3 - 3Q_2Q_1 + 2Q_1^3) + 3(Q_2 - Q_1^2)^2 \right]
\]  

(3.29)

where
\[ Q_N = \int_V \exp \left[ -\frac{U(x_1, x_2, \ldots, x_N)}{kT} \right] dr_1 \ldots dr_N \] (2.40)

Equation (2.38) reduces to:

\[ B = -2\pi L \int_0^\infty f_{12} r^2 dr \] (2.41)

where \( f_{12} = \exp(-U(r)/kT) - 1 \) is the Mayer function.

The evaluation of (2.39) is more difficult because of deviations from additivity. The potential energy of three atoms \( U(x_1, x_2, x_3) \) is formally the sum of the pairwise additive terms plus an extra term, the non-additive term, \( \Delta U(r_{12}, r_{23}, r_{31}) \). On evaluating (2.39):

\[ C = C_{\text{add}} + \Delta C \]

where \( C_{\text{add}} \) is the additive contribution to \( C \) and \( \Delta C \) is the non-additive term derived from \( \Delta U \).

\[ C_{\text{add}} = \frac{-1}{3V} \int \int \int f_{12} f_{13} f_{23} dr_1 dr_2 dr_3 \] (2.24)

\[ C = \frac{-1}{3V} \int \int \int [\exp(-\Delta U/kT) - 1] \times \exp \left[ -\left( \frac{U(r_{12}) + U(r_{13}) + U(r_{23})}{kT} \right) \right] dr_1 dr_2 dr_3 \] (2.43)

Some authors have neglected the \( \Delta C \) contribution in their comparison of the experimental and calculated third virial coefficients. This is not a valid procedure since Sherwood, De Rocco and Mason (1966a, 1966b) have shown that if \( \Delta U \) is expressed as the sum of both the non-additive dispersion and repulsion energies, the percentage error due to its neglect is of the order of 77% at 120 K for argon. This value falls to 20% at 240 K but even at relatively high temperatures (\( \approx 1200 \) K), remains about 4%.
With the knowledge of the theoretical expressions of B and C in terms of \( U(r_1, r_2) \) and \( \Delta U \), it is possible by comparison with experimental values taken over a temperature range, to fix the form of the interatomic potential. A full discussion of experimental methods is given by Mason and Spurling (1969).

The procedure is to obtain experimental values of B over as wide a range of temperatures as possible and, by using one of the analytical potentials to minimize the root-mean-square deviation, \( \text{rms} \), to obtain the optimum parameters. A limitation of this method that has been studied by Klein and Hanley (1968, 1969), is the insensitivity of the form of \( U(r) \) in the calculation of B over certain temperature ranges. If the experimental data falls within such a range, it is not possible to use it to distinguish between potential models. Keller and Zumino (1959) have found that only \( U^{\text{rep}} \) is determined uniquely, and that the potential well is only partially determined, i.e. its width can only be found as a function of its depth. For neon, argon, krypton, nitrogen and carbon dioxide, the B data in the range could be reproduced reasonably well with different shaped functions but all with the same integral:

$$\int_{a}^{b} U(r) dr$$

The insensitive temperature ranges in the determination of B are presented by Klein and Hanley (1968). For argon this is 239.6-1198 K and for krypton 742-1710 K.

The LJ equation gives the worst agreement with experimental results, particularly in the high temperature range. Kihara (1953) points out that the potential needs a wider well (i.e. \( n < 12 \)) but also the repulsive part of the curve is too "soft" (i.e. \( n > 12 \)). Toxvaerd and Praestgaard (1968), TP, have found that using the
Kingston (1974) C_6 value in the bireciprocal potential, with m = 6 and keeping $K_n$ and n as variables, gave an r.m.s. fit with n = 20 for argon and n = 18.0 for krypton. However, in spite of the lower r.m.s. compared with the LJ function, the repulsive region of the interatomic potential with n > 12 still gives poor agreement with atomic scattering data and TFD results (see fig. 2.1).

The three parameter equations, being more flexible than the LJ function, have given better results. A number of researchers have used these equations, particularly the "exp6". Probably the most important treatments are those due to Mason (1954, 1955), Sherwood and Prausnitz (1963, 1964), SP, and Toxvaerd and Praestgaard (1968). The SP method remains the most comprehensive since both B and C are calculated, and in the case of C taking account of the non-additivity in the dispersion interaction. Unfortunately SP used the low temperature virial coefficient data of Fender and Halsey (1962) which is inaccurate. The more recent work of TP used the same temperature range of experimental data, (84-800 K), but used the low temperature data of Weir, Wynn-Jones, Rowlinson and Saville (1967) in place of Fender and Halsey's. Experimental work by Byrne, Jones and Staveley (1968) gives good agreement with the findings of Weir et al (1967), but both showing marked disagreement with that data of Fender and Halsey (1962). The interesting point obtained from the TP work is that all the three parameter equations used, (i.e. the "exp6", Kihara and m-6 bireciprocal potential), gave almost the same interatomic well for argon and krypton. TP also accounted for quantum effects, (see Mason and Spurling 1969), which are negligible for krypton and only 2% of B for argon. However in the calculation of C, they have a larger effect and must be considered. TP calculated C for argon using the m-6 potential and corrected for ΔC arising from dispersion
forces. An m value in the range 18-20 gave agreement with experimental, confirming the conclusions of the B data analysis.

The Mason method is different because Corners (1948) procedure of using crystal data, (lattice energies and heats of sublimation), is used in conjunction with second virial coefficients and transport properties (in this case viscosity). The virial coefficient data used was limited in range to that available at the time. Also more recent measurements, (see Hanley and Childs 1968), of the coefficient of viscosity at high temperatures indicates that values obtained earlier are too low. The difficulty in using crystal data is that many-body effects become important, so the resulting potential is not truly a pair potential. The results of Mason (1954, 1955) and TP are shown in fig. 2.2 together with a number of other comparisons. The Mason result is widely different from the other equations. However, Mason's work has been extended to all the inert gases, whereas TP and SP results are for argon and krypton.

2.6 PAIR POTENTIAL PARAMETERS FROM GAS TRANSPORT DATA

The viscosity, thermal conductivity, self-diffusion coefficients and isotropic thermal diffusion factors are related to the interatomic potential through the collision integrals. A complete investigation of this procedure is given by Chapman and Cowling (1939).

Klein and Hanley (1968, 1969) have shown that the transport properties above also have an insensitive temperature range. The range is smaller than that of the virial coefficients and is smallest for the isotropic thermal diffusion factor. Since the thermal conductivity and viscosity coefficients are related to U(r) through the same collision integral, the parameters determined from these properties are not independent.
Fig. 2.2 Interatomic potential energy functions for the argon self-interaction

Key:  
- o - "exp6". Mason and Rice (1954)
--- Dymond and Alder (1969)
- x - "exp6" from SP
--- this work; Kingston $C_6$ with $c_1$ and $c_2$ optimized from the bulk second virial coefficients used by TP
- - - "exp6" from TP
The LJ or three parameter equations are not able to fit all of these properties well over a wide temperature range. They deviate at either low or high temperatures. This may be due to errors in the experimental data or to the fact that a more generalized interatomic potential function is required. Dymond and Alder (1969) have not restricted their own analysis of the transport properties of argon, including virial coefficients, to any analytical pair potential. By a multivariational method they determine a potential energy function that fits all the experimental data with a minimum of error. This numerical function is shown in fig. 2.2. It is considerably different from the other functions for argon, being broader and of smaller well depth than either of the functions determined by SP or TP. The asymptotic behaviour is not in agreement with Kingston's (1964) results, although as shown in fig. 2.1 it is in good agreement with the atomic scattering and TFD results. Dymond and Alder (1969) conclude that more accurate experimental data is required before constraints put on the potential by the analysis of the data do not arise because of inconsistent data.

2.7 ASYMPTOTIC LIMITS OF THE SEMIEMPIRICAL FUNCTIONS

A comparison of the short range limits has been illustrated in fig. 2.1. The long range interactions shown in fig. 2.2 are in some disagreement, especially when the asymptotic $c_6$ of (2.32b) or (2.29) are compared to the reliable values of Kingston (1964).

This problem has been overcome by Munn (1964) using the Boys-Shavitt potential. This gives $c_6$ values in agreement with Kingston's. It has been suggested by Kingston (1965) that the "exp6" and Kihara potentials cannot give the correct asymptotic Kingston $c_6$ values and at the same time show good agreement with virial coefficient work.
He constructed a potential consisting of a Kingston $c_6$ "tail" with an LJ potential well and repulsive component. This showed better agreement with the virial coefficient results.

The failure of the "exp6" may be ascribed to its limited flexibility. To investigate this further (2.34) may be used with $C = c_6$ from Kingston's work. Although the resulting potential function would exhibit the correct long range behaviour, the $c_6$ term may be inadequate in the region of the potential well because of the neglect of the induced multipole terms, e.g. induced dipole – induced quadrupole and higher interactions, and the possible failure of the $r^{-6}$ dependence (see §2.2.1).

Table 2.2 lists the results obtained in this work by equating $C = c_6$ from Kingston's work, and optimizing $c_1$ and $c_2$ in (2.34) to obtain the best agreement with second virial coefficients. The difference between the two sets of virial coefficient data used, was that the SP data included the Fender and Halsey (1962) low temperature work and TP replaced it with more reliable data (see §2.5). The values of $c_1$ and $c_2$ were obtained by a series of linear searches over a wide field to obtain a minimum in the r.m.s. deviation from experimental data. Newton's method of steepest descents was attempted but because of constraints on $c_1$ and $c_2$, failed to converge. The use of the Kingston $c_6$ value translates the potential energy curve and improves the agreement in the repulsive region (fig. 2.1 and 2.2).

The calculation of the Mayer function, discussed in Chapter 4, depends on the inert gas self-interaction. The ideal two-dimensional virial coefficient, $B_{2D}$, is related to $f_{12}$ as shown in fig. 2.3. At 85 K, $B_{2D}$ is mainly dependent on the negative loop of the curve determined from the potential well. Hence the calculation of $B_{2D}$ is not sensitive to the repulsive part of the potential energy curve.
Fig. 2.3, 2.4: Influence of attractive and repulsive contributions of the atomic interaction potential in the determination of the bulk-phase gas virial coefficients for argon at 85 and 800K using the "exp6" equation with parameters of SP: \( B = -2\pi \int_0^\infty g(r_{12}) dr_{12} \)

Fig. 2.3
\( T = 85K \)

Fig. 2.4
\( T = 800K \)
As shown in fig. 2.4 this is not the case at higher temperatures.

**TABLE 2.2** C<sub>6</sub> **VALUES**, TOGETHER WITH THE r.m.s. **DEViations FOR Ar** OBTAINED BY COMPARING DIFFERENT POTENTIAL FUNCTIONS WITH THE EXPERIMENTAL BULK PHASE SECOND VIRIAL COEFFICIENT DATA

<table>
<thead>
<tr>
<th>references</th>
<th>argon C&lt;sub&gt;6&lt;/sub&gt; /10&lt;sup&gt;-11&lt;/sup&gt; erg Å&lt;sup&gt;6&lt;/sup&gt;</th>
<th>krypton C&lt;sub&gt;6&lt;/sub&gt; /10&lt;sup&gt;-11&lt;/sup&gt; erg Å&lt;sup&gt;6&lt;/sup&gt;</th>
<th>r.m.s.&lt;sup&gt;a&lt;/sup&gt; /10&lt;sup&gt;-6&lt;/sup&gt; m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>r.m.s.&lt;sup&gt;b&lt;/sup&gt; /10&lt;sup&gt;-6&lt;/sup&gt; m&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mason (1955)</td>
<td>9.938</td>
<td>19.000</td>
<td>3.40</td>
<td>5.39</td>
</tr>
<tr>
<td>SP (1963)</td>
<td>7.372</td>
<td>16.050</td>
<td>0.51</td>
<td>2.29</td>
</tr>
<tr>
<td>TP (1968)</td>
<td>6.427</td>
<td>14.850</td>
<td>2.59</td>
<td>0.53</td>
</tr>
<tr>
<td>LJ (parameters from TP 1968)</td>
<td>12.768</td>
<td>26.640</td>
<td>2.02</td>
<td>3.22</td>
</tr>
<tr>
<td>Kingston (1964)</td>
<td>6.26</td>
<td>12.54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Barker and Leonard (1964)</td>
<td>6.38</td>
<td>12.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>this work</td>
<td>6.26</td>
<td>12.54</td>
<td>1.91</td>
<td>2.45</td>
</tr>
</tbody>
</table>

<sup>a</sup> Using the same data as SP  
<sup>b</sup> Using the same data as TP

In this work two sets of parameters for the "exp6" are used. The Mason (1954, 1955) parameters are available for all the inert gases, and the more reliable parameters of TP are also used for argon and krypton.

2.8 **THE ION-INERT GAS INTERACTION USING THE FROST AND WOODSON APPROXIMATION**

The ion-inert gas interaction potentials are known with less certainty than the inert gas self-interaction potentials. Even for the free ion-inert gas potential, little is known. For the case
when the ion is within a crystal, difficulties arise because of the effects of the environment of the ion. This is clearly seen from the nonadditivity of free ion polarizabilities to give the corresponding crystal polarizabilities (Pirenne and Kartheuser 1964). However an additivity rule may be applied such that $\alpha_{ab} = \alpha_a + \alpha_b$ where $\alpha_a$ and $\alpha_b$ are in general not the free polarizabilities. Although $\alpha_a$ and $\alpha_b$ may remain approximately constant within a family of salts, (i.e. of a particular crystal structure), they assume different values when the structure is altered, e.g. $\alpha_{Cl^-}$ in sodium chloride is different to $\alpha_{Cl^-}$ in magnesium chloride (Boswarva 1970). This problem may only be overcome by relating the properties of the ions to their physical environment. This is a complex problem that is discussed in §2.10.

A gross simplification is obtained if the Frost and Woodson (1958), FW, approximation is applied. This assumes that since the magnitude of the dispersion and repulsion forces are primarily dependent on the electron shells, ions are equivalent to inert gas atoms containing the same number of electrons. FW calculated the potential energy curve and the $r_m$ and $\varepsilon$ values for a number of alkali gas molecules using corresponding inert gas shell parameters for the ions. They found that the results were in good agreement with the observed $r_m$ and $\varepsilon$ values. Since for sodium chloride the neon parameters should overestimate the attraction forces for the sodium ion and the argon values underestimate for the chloride ion, the result may be fortuitous because of some error cancellation. However it did prove successful for the range of alkali halides that they considered.

In the present work, replacing the ions within the crystal by the corresponding inert gas core may not lead to error cancellation. This is shown in Table 2.3.

<table>
<thead>
<tr>
<th>system</th>
<th>( \frac{x_1 x_2}{(\alpha_1 x_1 + \alpha_2 x_2)} )</th>
<th>% error using FW approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺/Cl⁻</td>
<td>2.68</td>
<td>1.12</td>
</tr>
<tr>
<td>Ar/Ar</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>K⁺/Br⁻</td>
<td>3.81</td>
<td>4.99</td>
</tr>
<tr>
<td>Ar/Kr</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Rb⁺/Br⁻</td>
<td>6.51</td>
<td>6.91</td>
</tr>
<tr>
<td>Kr/Kr</td>
<td>6.06</td>
<td></td>
</tr>
<tr>
<td>Na⁺/Cl⁻</td>
<td>0.843</td>
<td>7.50</td>
</tr>
<tr>
<td>Ne/Ar</td>
<td>0.780</td>
<td></td>
</tr>
<tr>
<td>Na⁺/Ar</td>
<td>0.619</td>
<td>26.0</td>
</tr>
<tr>
<td>Cl⁻/Ar</td>
<td>3.855</td>
<td>31.4</td>
</tr>
<tr>
<td>K⁺/Ar</td>
<td>1.06</td>
<td>42.5</td>
</tr>
<tr>
<td>Cl⁻/Ar</td>
<td>3.86</td>
<td>31.3</td>
</tr>
</tbody>
</table>

For error cancellation to occur in the sums over the crystal, the following condition must be fulfilled:

\[
\sum_j \frac{C_{31}}{r_j^6} = \sum_k \frac{C_{32}}{r_k^6} \tag{2.44}
\]

where \( j \) labels the anion-inert gas distance

and \( k \) labels the cation-inert gas distance

and the subscripts:

1. anion
2. cation
3. inert gas
If (2.44) is evaluated for the sodium chloride lattice, error cancellation occurs in the region of the centre of the unit cell but over the individual ion positions error cancellation cannot be expected. The errors in these positions should be of the order of the individual ion-inert gas non-cancellation errors listed in Table 2.3.

2.9 THE COMBINATION RULES

As discussed in §2.1, the individual ion-inert interactions are required. Since there is no direct way to determine them, the combination rules that have proved successful for the mixed inert gas interactions, are adopted.

Dispersion theory suggests the following combination rule for C of (2.34):

\[ C_{12} = (C_{11}C_{22})^{\frac{1}{2}} \]  

(2.45)

where the subscripts refer to the atom types. Dalgarno's (1967) tabulation of C₆ for the mixed inert gas interactions, shows that (2.45) is correct to within 2%. Also Mason (1954, 1955) uses (2.45), and since his parameters for the "exp6" combined with the FW approximation are used in part of this work, it is consistent to use (2.45) here.

The remaining combination rules may be summarized:

\[ (c_{11})_{12} = \left[ (c_{11})_{11}(c_{11})_{22} \right]^{\frac{1}{2}} \]  

(2.46)

\[ (c_{22})_{12} = \frac{1}{2} \left[ (c_{22})_{11} + (c_{22})_{22} \right] \]  

(2.47)

Abrahamson (1969) has shown (2.46) and (2.47) to be correct to within 1%. This has been confirmed by Gaidziska and Nikulin (1970) and also by the inert gas scattering results of Amdur (1956). There is some doubt whether the resulting mixed potential will also be
accurate in the well region, but in the absence of a better method the combination rules should yield a useful approximation.

2.10 THE DETERMINATION OF INTERIONIC POTENTIAL PARAMETERS FROM CRYSTAL DATA

2.10.1 The Determination of the Dispersion Coefficients

Before the BM constants $c_1$ and $c_2$ for the ions can be determined, the $C_6$ constant is required. This was originally carried out by Mayer (1933). The problem is to obtain $\Delta$ and $a$ for the anion for use in (2.8). This was done by a lengthy analysis of optical information about the alkali halide crystals. The absorption spectrum of the alkali halides consists of two parts; the 2500 $\AA$ to 1000 $\AA$ region attributed to the anion, and the 400 $\AA$ region due to the cation. Only for sodium chloride, potassium chloride and potassium iodide was there sufficient range of absorption and dispersion information (i.e. the refractive index measured as a function of frequency). There was also a limited amount of data on the cation spectrum. The more recent work by Hajj (1966) confirms that there are still uncertainties regarding the cation $C_6$ value.

The details of the analysis will not be discussed. However two important approximations are made:

(i) The $a$ values of Pauling (1927) are used. These are the free ion values which are too large (Tessman, Kahn and Shockley 1953; Pirenne and Kartheuser 1964).

(ii) $\Delta_{\text{cation}} = 0.75 \times$ ionization energy. This is an arbitrary choice by Mayer (1933). In general Pitzer (1959) has suggested that $\Delta = 1.15 \times$ ionization energy for 2 electron systems and $\Delta = 2.25 \times$ ionization energy for sp closed shells. These figures are in agreement with the observation that replacing the "effective energy", $\Delta$, with the
corresponding ionization energy, leads to values of \( U^{\text{dis}} \) which are far too low.

To avoid this, Hajj (1966) uses Ruffa's (1963) "effective characteristic energies", (which are lower than Mayer's values), together with the Tessman, Kahn and Shockley (1953) polarizabilities, to calculate the cation self-interaction. The results of Mayer's and Hajj's analysis are shown in Table 2.4. The TP \( C_6 \) values were used for argon and the combination rules of 2.9 determined the corresponding ion-inert gas constant.

A number of other methods may be suggested to determine the interaction:

(i) The FW approximation may be used with the inert gas parameters from Mason (1955)

(ii) The SK equation may be adopted using the electron numbers of Wilson (1965) and crystal polarizabilities of Deltour (1971) and Landolt-Börnstein (1951). The electron numbers of the ions are taken as those for the corresponding inert gas core.

(iii) The KM equation may be applied by using the polarizabilities as in (ii) and the magnetic susceptibilities of Glick (1961) and Deltour (1967).

(iv) The KM equation may be assumed to give values consistently high such that:

\[
C_6(\text{Ion-Ar}) = C_6(\text{Ar-Ar}) \left( \frac{C_6(\text{ion-Ar})}{C_6(\text{Ar-Ar})} \right)_{\text{KM values}}
\]  

(2.48)

where the \( C_6(\text{Ar-Ar}) \) values of Kingston (1964) are used. The method will be called the Davis and Majee (1973).
procedure.

(v) The theoretical "effective energy" values of the ions, Ruffa (1963), may be used to calculate $C_6$(Ion-Ion) and using the Kingston $C_6$(Ar-Ar) value, the $C_6$(Ion-Ar) constant may be determined.

### TABLE 2.4 COMPARISON OF THE VARIOUS $C_6$ CONSTANTS FOR THE Ar-Na\(^+\) AND Ar-Cl\(^-\) INTERACTION

<table>
<thead>
<tr>
<th>method</th>
<th>discussion</th>
<th>$C_6/10^{-11}\text{erg}^{\text{erg}}$ Na(^+)-Ar</th>
<th>$C_6/10^{-11}\text{erg}^{\text{erg}}$ Cl(^-)-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>KM</td>
<td>(iii)</td>
<td>3.040</td>
<td>18.934</td>
</tr>
<tr>
<td>FW</td>
<td>(i)</td>
<td>2.939</td>
<td>9.937</td>
</tr>
<tr>
<td>SK</td>
<td>(ii)</td>
<td>1.431</td>
<td>9.706</td>
</tr>
<tr>
<td>DM</td>
<td>(iv)</td>
<td>1.467</td>
<td>9.137</td>
</tr>
<tr>
<td>Mayer</td>
<td>main text</td>
<td>1.025</td>
<td>8.521</td>
</tr>
<tr>
<td>Hajj</td>
<td>main text</td>
<td>1.787</td>
<td>6.354</td>
</tr>
<tr>
<td>Ruffa</td>
<td>(v)</td>
<td>2.041</td>
<td>13.543</td>
</tr>
</tbody>
</table>

The range of $C_6$ values is shown in Table 2.4. The $C_6$ constant obtained using Ruffa's $\Delta$ values appears to be closer to the KM limit. This indicates that the $\Delta$'s may be too high so that Hajj's result overestimates the Na\(^+\)-Ar interaction.

Since the KM and the Mayer results indicate opposite limiting values of $C_6$ for the ion-inert gas interaction, they are used in the gas-solid virial coefficient computations in Chapter 4.

#### 2.10.2 The Determination of the BM Repulsion Constants

With information about the dispersion constants of the ions, the repulsion constants may be obtained from an analysis of bulk crystal
data. The lattice energy of a crystal may be written in the form of sums over the interionic interactions. The Born treatment commonly used does not make any attempt to determine any of the individual potential energy contributions to the lattice energy, $W_L$, but utilizes the knowledge of the various contributions and their functional form. This is usually done by fitting the model expression of the lattice energy to the equation of state of the crystal and its volume derivatives at constant temperature and pressure. Different equations of state have been suggested. The main difficulty is taking into account the contribution of the lattice vibration to the free energy of the solid. One accurate method is to assume that this vibrational energy of the solid is purely temperature dependent. This gives the Hildebrand equation of state (see Tosi 1964). In this way the volume derivatives of the equation of state are directly related to the compressibility of the crystal.

The interaction between two single ions is conveniently written in the form:

$$U_{\text{rep}} = \beta_{+ -} b_+ b_- \exp(-r/p)$$

(2.49)

where the subscripts indicate the ion charge and $\beta_{+ -}$ is a Pauling coefficient given by:

$$\beta_{pp'} = 1 + \left( \frac{Z_p}{n_p} \right) + \left( \frac{Z_{p'}}{n_{p'}} \right)$$

(2.50)

where $Z_p$ and $n_p$ are the valence and number of outer shell electrons on the $p$th ion. The repulsion parameters $b_+$ and $b_-$ are expressed:

$$b_p = b_0 \exp(\frac{r_p}{\rho})$$

(2.51)

where $r_p$ is the basic ionic radius (sometimes called the characteristic length). The crystal radii, $R_-$ and $R_+$, of the ions may be
obtained from the basic radii (see Tosi 1964):

\[
\begin{align*}
R_- + R_+ &= R_{12} \\
R_- - R_+ &= \rho \ln(b_-/b_+) 
\end{align*}
\]  \hfill (2.52)

where \(R_{12}\) is the experimental interionic distance.

Using this model, the contribution of the repulsion energy to the lattice energy may be written:

\[
W^{\text{rep}} = M_B b \exp[(r_+ + r_- - r)/\rho] + \frac{1}{2} M'_b [\beta_{++} \exp(2r_+ / \rho) + \\
\beta_{--} \exp(2r_- / \rho)] \exp(-r^1 / \rho) \hfill (2.53)
\]

where

- \(M\): number of first neighbours
- \(M'\): number of second neighbours
- \(r_+\): basic radius of cation
- \(r_-\): basic radius of anion
- \(r\): nearest neighbour distance
- \(r^1\): second nearest neighbour distance
- \(\rho\): "hardness" parameter

Hence the total lattice energy may be obtained:

\[
W_L = -\frac{a_R e^2}{r} - \frac{c_R}{r^6} - \frac{D_R}{r^8} + M_B b \exp(\frac{r_+ + r_- - r}{\rho}) + \frac{1}{2} M'_b \left[ \beta_{++} \exp(\frac{2r_+}{\rho}) + \beta_{--} \exp(\frac{2r_-}{\rho}) \right] \exp(-\frac{r^1}{\rho}) \hfill (2.54)
\]

where

- \(a_R\): Madelung constant
- \(r\): nearest neighbour distance
- \(C_R\): \(c_+ S^2_R(r^-) + \frac{1}{2}(c_{++} + c_{--}) S^2_R(0) \hfill (2.55)\)
- \(D_R\): \(d_+ S^2_R(r^-) + \frac{1}{2}(d_{++} + d_{--}) S^2_R(0) \hfill (2.56)\)
\( c_{ij}, d_{ij} \): the dispersion coefficients for the i and j ion interactions

\( S_R \): the lattice sums for the crystal lattice. For a sodium chloride type lattice (Tosi 1964) –

\[
S_R^6(0) = 1.8067 \quad S_R^6(0) = 0.8001 \\
S_R^6(r) = 6.5952 \quad S_R^6(r) = 6.1457
\]

By applying (2.54) into the Hildebrand equation of state:

\[
\frac{dW_L}{dv} = -P + \frac{T\beta}{K}
\]  \( \text{(2.57)} \)

\[
V \frac{d^2W_L}{dv^2} = \frac{1}{K} + \frac{T}{K^2} \left[ \frac{\partial K}{\partial T} + \frac{\beta}{K} \frac{\partial T}{\partial P} \right]
\]  \( \text{(2.58)} \)

where \( \beta \): the coefficient of thermal expansion

\( P \): hydrostatic pressure

\( K \): isothermal compressibility

\( V \): volume of the crystal (\( = 2\pi r^3 \) where \( n \) is the number of molecules in the crystal), after some lengthy algebra the following two equations are obtained:

\[
r = \rho \ln \left\{ 6\beta_+ \frac{b_+ b_- r}{\rho} \left[ 1 + \sqrt{2} \left( \frac{\beta_+ b_+}{\beta_+ b_-} + \frac{\beta_- b_-}{\beta_+ b_+} \right) \exp \left[ (1 - \sqrt{2}) \frac{r}{\rho} \right] \right] \right\} / T
\]  \( \text{(2.59)} \)

\[
\frac{r \frac{\Gamma}{\rho \sigma} - 1}{\sqrt{2} \frac{r \frac{\Gamma}{\rho \sigma} - 1} = -\sqrt{2} \left( \frac{\beta_+ b_+}{\beta_+ b_-} + \frac{\beta_- b_-}{\beta_+ b_+} \right)
\]  \( \text{(2.60)} \)

with \( \Gamma = \frac{\alpha R e^2}{r} + \frac{6c_R}{r^6} + \frac{8d_R}{r^8} - \frac{6\pi^2\beta T}{K} \) \( \text{(2.61)} \)

\[
\sigma = \frac{2\alpha R e^2}{r} + \frac{6d_R}{r^6} + \frac{72d_R}{r^8} + \frac{18\pi^2\beta T}{\rho} \left\{ 1 + \frac{T}{K} \left[ \frac{\alpha K}{\beta T} \right] \right\}
\]  \( \text{(2.62)} \)
Since it is impossible to determine $b_+$ and $b_-$ uniquely for both ions within each salt because there are more unknowns than possible equations, it is assumed that the $b_+$ and $b_-$ values are constant for each type of ion within a particular crystal structure. This is analogous to the known additivity of ionic polarizabilities within a crystal structure, discussed in §2.8. In this treatment, only the alkali halides with the sodium chloride structure are included in the analysis. Hence experimental values of $r$, $K$, $\beta$, $\frac{1}{T} \frac{\partial K}{\partial T}$, $-\frac{1}{K} \frac{\partial (2K)}{\partial T}$ are available, (Tosi 1964), for 17 salts. The problem is to determine 9 $b_+$ values and the corresponding 17 $\rho$ values. Tosi (1964) has shown that both the $b_+$ and $\rho$ values may be determined from the data by using (2.59) and (2.60). However the uncertainties in some of the crystal data make the calculation of individual $\rho$ values questionable. In fact, as shown in Table 4.1, the derived atom-ion potential energy functions are not sensitive to whether one $\rho$ is common to all the salts or individual $\rho$ values are determined. Further to this the agreement of calculated and experimental cohesive energies for the alkali halides is satisfactory by either method. Tosi (1964) also concludes that since there are no consistent deviations between the experimental and calculated cohesive energies, additional attractive forces to account for covalent bonding are not required.

The method used here is an iterative one involving the following stages:

(i) Initialization of $b_-$ and $b_+$ values for each of the ions considered. The $\rho$ values are then computed from (2.60) for each of the 17 crystals.

(ii) Calculation of the average value of $\rho$. 
(iii) The redetermination of the $b_+$ and $b_-$ values using the common $\rho$ value. This is achieved by calculating $r$ from (2.59) by a numerical method. The procedure is repeated for each of the 17 salts and the values of $r$ then compared to the experimental, and a minimum r.m.s. deviation solution is obtained by an appropriate optimisation method.

(iv) The new values of $b_+$ and $b_-$ determined in (iii) are used to calculate a new average $\rho$.

(v) Stage (iii) is repeated. The process is continued until there is no change in $\rho$.

This method has been used by Huggins and Mayer (1933) and Tosi (1964) with the Mayer (1933) $c_{ij}$ and $d_{ij}$ values in (2.55) and (2.56). Since these are likely to be too low, two other models were also adopted in this work. The KM and SK equations described in §2.10.1 were used to recalculate $c_{ij}$ values. The $d_{ij}$ constants were equated to zero because no information was available for the corresponding inert gas values that would be required in the combination rules (§2.9). The r.m.s. deviation minimization was obtained using the simplex method of Nelder and Mead (1965). This was developed by the Nottingham Algorithm Group, (NAG), and was on file during the program execution. The method is a rugged one that is less prone to converging on local minima. The program starts off with a simplex, in this case 10 points in the 9-dimensional $b_\rho$ space. The highest point is continually replaced by reflecting that point in the hyper-plane of the remaining points. The simplex adapts itself to the local landscape since it can move quickly down a gradual incline, change direction and contract in the region of the minimum. Although local minimum were encountered, a number of runs with different starting $b_+$ and $b_-$ sets were used. The final r.m.s. devia-
tions were 0.0006 nm, 0.0007 nm and 0.0008 nm for the potential sets A, B and C of Table 2.5.

The interionic BM parameters can be obtained from the \( b_+ \) and \( b_- \) values that are presented in Table 2.5. The results indicate that the repulsion constants are unique for a set of \( c_{ij} \) values. The method of arbitrarily combining the Huggins and Mayer (1933) constants with any dispersion constants other than Mayer's (1933) is not valid.
TABLE 2.5 BORN REPULSIVE PARAMETERS $b_+$, $b_-$ AND $c_2$

The $C$ values were determined from the Slater-Kirkwood and Kirkwood-Müller formulae as described in the text.

<table>
<thead>
<tr>
<th>set reference</th>
<th>C value</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
<th>F$^-$</th>
<th>Cl$^-$</th>
<th>Br$^-$</th>
<th>I$^-$</th>
<th>$c_2$ /nm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fumi and Tosi (1964)</td>
<td>57.86</td>
<td>157.2</td>
<td>364.1</td>
<td>530.8</td>
<td>795.5</td>
<td>133.7</td>
<td>446.8</td>
<td>650.9</td>
<td>1132</td>
<td>29.50</td>
</tr>
<tr>
<td>B</td>
<td>Slater-Kirkwood</td>
<td>57.44</td>
<td>158.3</td>
<td>353.0</td>
<td>507.7</td>
<td>732.1</td>
<td>127.5</td>
<td>422.9</td>
<td>626.8</td>
<td>1064</td>
<td>29.07</td>
</tr>
<tr>
<td>C</td>
<td>Kirkwood-Müller</td>
<td>46.51</td>
<td>131.0</td>
<td>293.1</td>
<td>425.4</td>
<td>635.0</td>
<td>121.5</td>
<td>391.0</td>
<td>585.5</td>
<td>1023</td>
<td>27.32</td>
</tr>
</tbody>
</table>

$\text{b}_+, \text{b}_-/(\text{kJ mol}^{-1})^{1/2}$
CHAPTER 3

SINGLE GAS ATOM-SURFACE INTERACTIONS

3.1 INTRODUCTION

The surface of an ideal crystal is a homotattic area with an intrinsic heterogeneity due to the atomic nature of the surface. Thus the potential field experienced by the adsorbed atom may be expected to be structured with some relation to the underlying crystal lattice. The state of the adsorbate will depend upon the structure of this potential field. If the minimum potential barrier to translation across the crystal surface, $V^0$, is much greater than the average energy of the adsorbed atom, then the adsorbate will be effectively localized at a point on the surface. As $V^0$ decreases, the degree of mobility is expected to increase.

The potential field experienced by an adsorbed atom may be calculated by a summation of the single inert gas-ion interactions as discussed in Chapter 2. The difficulties associated with determining the relevant pairwise potentials have already been discussed and limiting models constructed. Since the ions within the surface and bulk crystal are electrically charged, an electrostatic potential field exists above the surface. This will increase the adsorption potential through an induced dipole-field interaction. Further to this, the total field will be dependent on the exact structure of the surface. Verwey (1946) originally calculated the surface distortion, (here called the surface relaxation), of the ions due to

† homotattic is a term used by Ross and Olivier (1964) to describe a uniform surface. This is a surface that gives rise to a potential energy field that is both regular and periodic in structure.
the unsymmetrical potential field in the crystal at the interface. Later calculations by Benson, Freeman and Demsey (1963) have shown that the relaxation of the ions is important. This effect is considered in the present calculations.

It is difficult experimentally to investigate the region of the isotherm where single atom-surface interactions are important. This is because real crystals are in general not perfect and may contain a number of defects, called heterogeneities, discussed in Chapter 5. Hence since this region, at liquid nitrogen adsorption temperatures, occurs at low pressures, the effects of high energy heterogeneities are most obvious. However the present investigation will give a better understanding of the adsorbate state which is important when analysing experimental isotherms. This is shown by the recent measurements by Ross and Hinchen (1970) and Jackson and Davis (1974) of argon adsorbed on cubic sodium chloride. The latter used a localized model to analyse the surface quality of their samples and the former a mobile model. Both groups of researchers claimed highly homogeneous samples.

3.2 THE SURFACE ELECTROSTATIC FIELD

3.2.1 Alternate Ion Array Field

The most obvious method to calculate the electrostatic potential, \( V \), at a position \( \mathbf{r} \) above the surface, is by a direct summation of the contributions from each of the ions within the lattice. Since the terms in this sum are inversely proportional to the distance of the ions from the position \( \mathbf{r} \), the sum is only slowly convergent. This was overcome by Madelung (1918) and independently by Ornstein and Zernike (1918) and later by Ewald (1921). The method used here is an adaption of that first presented by Born (1923) and later used for
the calculation of crystal surface cohesion by Lennard-Jones and Dent (1928).

Fig. 3.1 Coordinate Systems Used in §3.2.1 and §3.2.2

The origin is taken as shown in fig. 3.1, with the surface plane, \( z = 0 \), passing through the centre of the outermost surface atoms. The z-axis of the set of coordinates, of which the surface plane is the xy plane, is normal to the surface. Where convenient the x and y lengths are expressed in reduced units:

\[
\begin{align*}
s_1 &= \frac{x}{a} \\
s_2 &= \frac{y}{b} \\
s_3 &= \frac{z}{c}
\end{align*}
\]

(3.1) for a unit cell \((a \times b \times c)\). In general \(a, b\) and \(c\) are the periodicities of the crystal structure in the directions of the three rectangular axes.
The method involves representing the alternate ion array in terms of a double Fourier series and from this, writing a general expression for the potential function. The unknown parameters in this function can be obtained with the aid of the Laplace equation and Gauss's Law.

The charge density distribution may be represented by a double Fourier series:

\[ \rho(s_1, s_2) = \sum_{\varepsilon_1, \varepsilon_2} p_{\varepsilon_1 \varepsilon_2} \exp[i2\pi(\varepsilon_1 s_1 + \varepsilon_2 s_2)] \]  

where \( \rho(s_1, s_2) \) is the charge density at \((s_1, s_2, 0)\)

\( \varepsilon_1, \varepsilon_2 \) are integers

\( p_{\varepsilon_1 \varepsilon_2} \) are the Fourier coefficients to be determined.

The prime to the summation indicates that the constant, \( p_{00} \), is not included in the sum. Since the mean charge density over one unit cell is zero. (The mean of the function over its period is always given by the constant term in the expansion.)

The potential is similarly periodic:

\[ V_{\varepsilon_1 \varepsilon_2} = f_{\varepsilon_1 \varepsilon_2}(z) \exp[i2\pi(\varepsilon_1 s_1 + \varepsilon_2 s_2)] \]  

where: \( f_{\varepsilon_1 \varepsilon_2}(z) \) are the coefficients

\( V_{\varepsilon_1 \varepsilon_2} \) must also be a solution to Laplace's equation

\[ \nabla^2 V = 0 \]  

A fundamental theorem in partial differential equations states that if \( V_{\varepsilon_1 \varepsilon_2} \) is a solution to a linear homogeneous differential equation, the linear combination of such solutions is also a solution, hence
in its most general form:

\[ v = \sum_{g_1, g_2}^{\infty} \frac{\epsilon_{g_1} \epsilon_{g_2}}{g_1 g_2} \]  

(3.5)

hence:

\[ v = \sum_{g_1, g_2}^{\infty} \frac{\epsilon_{g_1} \epsilon_{g_2}}{g_1 g_2} \frac{d}{dz} \frac{f_{g_1 g_2}(z) \exp[-i2\pi(g_1 s_1 + g_2 s_2)]}{a^2} \]  

(3.6)

Substituting (3.6) into (3.4) gives:

\[ \frac{d^2 v}{dx^2} = \frac{4\pi^2 \epsilon_{g_1}^2}{a^2} f_{g_1 g_2}(z) \exp[i2\pi(g_1 s_1 + g_2 s_2)] \]  

(3.7)

and similarly for the y and z derivatives to yield

\[ \exp[i2\pi(g_1 s_1 + g_2 s_2)] \left[ \frac{\partial^2}{\partial z^2} \frac{f_{g_1 g_2}(z)}{a^2} - \frac{f_{g_1 g_2}(z)}{b^2} \left( \frac{4\pi^2 \epsilon_{g_1}^2}{a^2} + \frac{4\pi^2 \epsilon_{g_2}^2}{b^2} \right) \right] = 0 \]  

(3.10)

The auxiliary equation (see Boas 1966) is:

\[ \left[ \frac{\partial^2}{\partial z^2} - 4\pi^2 (s_1^2 + s_2^2) \right] f_{g_1 g_2}(z) = 0 \]  

(3.11)

where

\[ D \equiv \frac{\partial^2}{\partial z^2} \]

The general solution becomes:

\[ f_{g_1 g_2}(z) = c \frac{\epsilon_{g_1} \epsilon_{g_2}}{g_1 g_2} \exp(gz) + c' \frac{\epsilon_{g_1} \epsilon_{g_2}}{g_1 g_2} \exp(-gz) \]  

(3.12)

where

\[ g = \frac{2\pi}{a^2 + b^2} \]  

(3.13)

Since \( \lim_{z \to \infty} V(z) = 0 \) then \( c' = 0 \) for all \( g_1 \) and \( g_2 \). Hence the
coefficients become:

\[ f(z) = c \varepsilon_1 \varepsilon_2 \exp(-g z) \]  
(3.14)

Substituting (3.14) into (3.3):

\[ \frac{V}{\varepsilon_1 \varepsilon_2} = c \varepsilon_1 \varepsilon_2 \exp(-g z) \exp[i 2\pi (s_1 + s_2)] \]  
(3.15)

Further boundary conditions are now required to solve for \( c \varepsilon_1 \varepsilon_2 \).

Considering the surface charge density, then a element \( dx \cdot dy \) of the surface encloses a charge \( \rho(x,y) \cdot dx \cdot dy \). From Gauss's theorem \[ \int_F \cdot dA = 4\pi \rho(x,y) \cdot dx \cdot dy \] where \( A \) is the area of the surface and \( F \) the electric field vector. This integral becomes \[ \int_F \cos \theta dA \] where \( \theta \) is the angle between the field vector and the normal to the surface plane (\( \theta = 180^\circ \) if \( \rho(x,y) \) is positive in \( dx \cdot dy \)). Hence

\[ \lim_{z \to 0} \frac{3V}{\varepsilon_1 \varepsilon_2} = -c \varepsilon_1 \varepsilon_2 \exp[i 2\pi (s_1 + s_2)] \]  
(3.18)

A comparison of (3.18) and (3.2) yields:

\[ c \varepsilon_1 \varepsilon_2 = \frac{2\pi \rho(x,y) / \varepsilon}{\varepsilon_1 \varepsilon_2} \]  
(3.19)

hence:

\[ V = 2\pi \int_{\varepsilon_1 \varepsilon_2}^{\varepsilon_1 \varepsilon_2} \rho(x,y) \exp(-g z) \exp[i 2\pi (s_1 + s_2)] \]  
(3.20)

To obtain a particular solution, the expansion coefficients
are required. The method used here is different from that adopted by Leonard-Jones and Dent (1928). Since the lattice is assumed to consist of point charges, the density function is not easily represented. However, it is single valued in the period with a finite number of maximum and minimum and a finite number of discontinuities, thus fulfilling Dirichlet’s conditions (Boas 1966) and therefore may be represented by a Fourier series. For a single ion array in the \( s_1 \) direction, the charge density may be expressed:

\[
\rho(x) = \sum_{m} c_m \exp(2\pi i s_1 m)
\]

(3.21)

where

\[
c_m = \frac{1}{a} \int_{0}^{a} \rho(x) \exp(i2\pi mx/a) dx
\]

(3.22)

This may be expressed:

\[
c_m = \frac{1}{a} \int_{0}^{h} \delta(x) \exp(-i2\pi mx/a) dx + \frac{1}{a} \int_{a/2}^{(a/2)+h} \delta(x) \exp(-i2\pi mx/a) dx
\]

(3.23)

Since \( \rho(x) = 0 \) in the range:

\[ h < x < a/2 \quad \text{and} \quad (a/2 + h) < x < a \]

and \( \delta(x) \) is a Dirac-delta function with the property:

\[
\int_{0}^{h} \delta(x) dx = 1 \leftrightarrow \delta x = 1/h
\]

Equation (3.23) may be evaluated to give:

\[
c_m = \frac{1}{a} - \frac{1}{a} \exp(im\pi)
\]

(3.24)

Hence:

\[
\rho(x) = \sum_{m} \frac{1}{a} \left[ 1 - \exp(-im\pi) \right] \exp(i2\pi ms_1)
\]

(3.25)
Similarly:
\[
\rho(y) = \int_{-\infty}^{\infty} \frac{1}{b}[1 - \exp(-i\pi)]\exp(i2\pi ls_2)\exp(-i\pi)  \tag{3.26}
\]

Now \(\rho(x)\) and \(\rho(y)\) are based on arrays of single charges. They may be combined to give the two-dimensional charge density:
\[
\rho(x,y) = \rho(x)\rho(y)Q  \tag{3.27}
\]

where \(Q\) is the charge on each of the ions. Applying (3.25) and (3.26) yields:

\[
\rho(x,y) = \sum_{l} \sum_{m} \frac{Q}{ab}[1 - \exp(-i\pi)] \exp(-im\pi) \exp(i2\pi ls_2) \times \exp(i2\pi ms_1)  \tag{3.28}
\]

hence
\[
\rho_{g_1g_2} = \frac{Q}{ab}[1 - \exp(-ig_1\pi)] \exp(-im\pi) \exp(i2\pi ls_2) \tag{3.29}
\]

Substituting (3.29) into (3.20) yields:

\[
V = 2\pi \sum_{g_1g_2} \frac{Q}{ab} \exp(-g_2\pi) \exp(i2\pi(g_1s_1 + g_2s_2)) [1 - \exp(-ig_1\pi)] \times [1 - \exp(-ig_2\pi)]  \tag{3.30}
\]

The last two terms in (3.30) may be expanded:

\[
D(g_1, g_2) = [1 - \exp(i\pi g_1)] [1 - \exp(-i\pi g_2)]
\]

\[
\leftrightarrow = 1 - \cos \pi g_1 \cos \pi g_2 + \cos \pi (g_1 + g_2)  \tag{3.31}
\]

An examination of (3.31) shows that:

\[
\sum_{g_1 \text{even}} D(g_1, g_2) = \sum_{g_1 \text{odd}} D(g_1, g_2) = \sum_{g_1 \text{even}} D(g_1, g_2) = 0  \tag{3.32}
\]

\[
\sum_{g_2 \text{even}} D(g_1, g_2) = \sum_{g_2 \text{odd}} D(g_1, g_2)
\]
hence since \( \sum_{g_1 \text{odd}, \; g_2 \text{odd}} D(g_1, g_2) = 4 \), (3.30) becomes:

\[
V = \frac{8\pi Q}{ab} \sum_{g_1, g_2 \text{ odd}} \frac{1}{g} \exp(-gz) \exp\left[i2\pi\left(g_1 s_1 + g_2 s_2\right)\right]
\]  

Equation (3.33) gives the electrostatic potential due to the surface layer. The total electrostatic potential may be obtained by a summation of all the contributions from each layer in the crystal. This may be achieved by writing:

\[
z_n = z + nc/2
\]  

Separating the \( z \) dependent term in (3.33), substituting \( z_n \) of (3.34) and summing over the entire crystal:

\[
A(z) = \sum_{n=0}^{+\infty} \exp\left[-g(z + nc/2)\right]
\]  

Equation (3.35) is a geometric series which may be replaced by:

\[
A(z) = \frac{\exp(-gz)}{1 + \exp(-gc/2)}
\]  

yielding:

\[
V(r) = \frac{8\pi Q}{ab} \sum_{g_1, g_2 \text{ odd}} \frac{1}{g} \exp(-gz) \cos\left[2\pi\left(g_1 s_1 + g_2 s_2\right)\right]
\]  

For a cubic lattice \( a = b = c \). The \( x, y \) and \( z \) components of the electric field may be obtained from the partial derivatives of \( V(r) \):

\[
F_x = -\frac{\partial V(r)}{\partial x} = \frac{16\pi Q}{a^3} \sum_{g_1, g_2 \text{ odd}} \frac{1}{g} \exp(-gz) \sin\left[2\pi\left(g_1 s_1 + g_2 s_2\right)\right]
\]  

(3.38)
An analogous expression to (3.38) may be obtained for \( F_y \).

\[
F_y = \frac{8\pi Q}{a^2} \sum_{\text{odd}} \frac{\exp(-g z)}{\varepsilon_1 \varepsilon_2 \left[1 + \exp(-g a/2)\right]} \cos[2\pi(g_1 s_1 + g_2 s_2)]
\]  

(3.39)

where 

\[
g = \frac{2\pi}{a} \left( g_1^2 + g_2^2 \right)^{1/2}
\]

The field components may be converted to MKS units, \((\text{Vm}^{-1})\), by dividing by \(4\pi\varepsilon_0\) where \(\varepsilon_0\) is the permittivity of a vacuum.

The corresponding electrostatic contribution to the potential field may be obtained knowing the polarizability, \(\alpha\), of the atom

\[
U^e = -\alpha \left| \mathbf{\varepsilon} \right|^2 /2
\]  

(3.40)

For computing purposes this may be written in the final form:

\[
U^e = -\frac{32\pi^2 a^2}{4} \sum_{n} [\varepsilon_z + \varepsilon_y + \varepsilon_x]
\]  

(3.41)

where

\[
\varepsilon_z = \left( \sum_n S_{nz} \varepsilon_{n2} \sum' \cos[2\pi(g_1 s_1 + g_2 s_2)] \right)^2
\]  

(3.42)

\[
\varepsilon_x = 4\pi^2 \left( \sum_n S_{nx} \varepsilon_{n2} \sum' g_1 \sin[2\pi(g_1 s_1 + g_2 s_2)] \right)^2
\]  

(3.43)

\[
\varepsilon_y = 4\pi^2 \left( \sum_n S_{ny} \varepsilon_{n2} \sum' g_2 \sin[2\pi(g_1 s_1 + g_2 s_2)] \right)^2
\]  

(3.44)

with 

\[
S_{nx} = \frac{\exp(-g* z*)}{[1 + \exp(-g* a/2)]g^*}
\]  

and 

\[
S_{nz} = g^* S_{nx}
\]

where \(z^* = z/a\) and \(g^* = ga\); \(n\) labels all the \(g_1, g_2\) values giving the same \(g^*\). This can be seen by writing \(g^* = 2\pi(g_1^2 + g_2^2)^{1/2}\). The summation over \((g_1 g_2)\) is for the individual \(g_1, g_2\) combinations that
Fig. 3.2 The z-component of the electric field at z = 3.0 Å above an ideal (100) sodium chloride surface

Units: V m\(^{-1}\)

Key: 
\[ \text{Na}^+ \]
\[ \text{Cl}^- \]
Fig. 3.3 Contour map of the electric field (V m⁻¹) at 3 Å above the surface plane of (100) sodium chloride. The electric field at the normal midcell position is zero.

Key:
- Na⁺
- Cl⁻
give a particular \( n \). As with (3.38) and (3.39) the \( g_1 \) and \( g_2 \) integers may only take odd values.

This result was tested in two stages. Equation (3.25) for \( \rho(x) \) was evaluated in the form:

\[
\rho(x) = \sum_{m=1}^{\infty} \frac{2}{a(1 - \cos \theta m)} \cos(2\pi m x) 
\]

(3.45)

The expansion was calculated at different values of \( x \) in the interval \( x = 0 \) to \( x = a \). The correct form of the density function was obtained. Secondly the final equations for \( F_z \), \( F_x \) and \( F_y \) were evaluated at different values of \( z \). The result for \( F_z \) at \( z = 3a \) is shown in fig. 3.2. These values may be converted to e.s.u. units by multiplying by a factor of \( 3 \times 10^4 \). The \( F_z \) quantities were in agreement with those of Lennard-Jones and Dent (1928). The field modulus also showed the correct symmetry (see fig. 3.3). The majority of previous researchers, including Hayakawa (1957b), have only used the \( z \) component of the field to calculate (3.40). A comparison of fig. 3.2 and fig. 3.3 shows that this neglect could result in substantial errors since the total field is only zero at the centre of the unit cell and not along the line perpendicular to the centre of the lattice edge.

Convergence to the fourth significant figure in \( U^0 \) was obtained by using the first four terms in (3.42), (3.43) and (3.44) i.e.

\[
|g_1| = 1 \quad |g_2| = 1 \quad (n = 1 \text{ term}); \quad |g_1| = 1 \quad |g_2| = 3 \quad (n = 2 \text{ term});
\]

\[
|g_1| = 3 \quad |g_2| = 3 \quad (n = 3 \text{ term}); \quad |g_1| = 3 \quad |g_2| = 5 \quad (n = 4 \text{ term}).
\]

3.2.2 Single Ion Array Field

The method developed in §3.2.1 is only appropriate with an alternate ion array such as the ideal sodium chloride lattice. When the
surface is allowed to relax, (see §3.6.3), the cations and anions are displaced perpendicular to one another. Hence the expansion of $\rho(x,y)$ in §3.2.1 is no longer valid. This problem can be overcome by calculating the field due to an array of identically charged points. The total field may then be found by summing the separate contributions from the cation and anion arrays. This method is more general than that developed in §3.2.1 but unfortunately is more demanding on computer resources.

The method outlined here follows that used in the previous section. The charge density of the two-dimensional lattice of identical charges becomes:

$$\rho(x,y) = \frac{Q}{ab} + \frac{Q}{ab} \sum_{g_1} \exp(i2\pi g_1 s_1) + \frac{Q}{ab} \sum_{g_2} \exp(i2\pi g_2 s_2)$$

$$+ \frac{Q}{ab} \sum_{g_1} \sum_{g_2} \exp[i2\pi(s_1 g_1 + s_2 g_2)]$$

(3.46)

where 'a' and 'b' are the lattice periods in the directions of $x'$ and $y'$ (fig. 3.1). This means that the coordinate system is rotated through 45 degrees, so all the ions can be accounted for in two separate summations.

The potential may be written in the form:

$$V = \sum_{g_1 g_2} f(z) \exp[i2\pi(s_1 g_1 + s_2 g_2)]$$

(3.47)

where the sum includes a constant term since the mean charge density is no longer zero. If the method of solving the Laplace equation is followed to determine $f_{g_1 g_2}$, the result of Madelung (1918) is obtained:
\[
V = \frac{2Q}{a} \sum_{g_1=1}^{+\infty} \frac{1}{g_1} \cos(2\pi s_1 g_1) \exp(-2\pi g_1 z) + \frac{2Q}{b} \sum_{g_2=1}^{+\infty} \frac{1}{g_2} \cos(2\pi s_2 g_2) \exp(-2\pi g_2 z)
\]
\[
+ \frac{8\pi Q}{ab} \sum_{g_1=1}^{+\infty} \sum_{g_2=1}^{+\infty} \frac{1}{g} \exp(-g \zeta) \cos(2\pi g_1 s_1) \cos(2\pi g_2 s_2) - \frac{2\pi Q z}{ab} \quad (3.48)
\]

where \( g = 2\pi \left( \left( \frac{s_1}{a} \right)^2 + \left( \frac{s_2}{b} \right)^2 \right)^{1/2} \)

The summation over the layers in the lattice may be performed as before. However, in the present calculation, this method is only used for calculating the electric field due to the relaxed surface layers. In this case, the summation is over a finite number of layers. In this instance, the components of the field become:

\[
F^+ = \frac{8\pi Q}{a^2} \sum_{\lambda=1}^{n} \sum_{g_1=1}^{+\infty} \sum_{g_2=1}^{+\infty} \exp(-z g) \cos(2\pi g_1 s_1) \cos(2\pi g_2 s_2)
\]
\[
+ \frac{4\pi Q}{a^2} \sum_{\lambda=1}^{n} \sum_{g_1=1}^{+\infty} \exp(-\frac{2\pi z}{a} g_1) \cos(2\pi g_1 s_1)
\]
\[
+ \frac{4\pi Q}{a^2} \sum_{\lambda=1}^{n} \sum_{g_2=1}^{+\infty} \exp(-\frac{2\pi z}{a} g_2) \cos(2\pi g_2 s_2) \quad (3.49)
\]

and

\[
F^+ = \frac{8\pi Q}{a^3} \sum_{\lambda=1}^{n} \sum_{g_1=1}^{+\infty} \sum_{g_2=1}^{+\infty} \exp(-g \zeta) \sin(2\pi g_1 s_1) \cos(2\pi g_2 s_2)
\]
\[
+ \frac{4\pi Q}{a^2} \sum_{\lambda=1}^{n} \sum_{g_1=1}^{+\infty} \exp(-\frac{2\pi z_1}{a} g_1) \sin(2\pi g_1 x) \quad (3.50)
\]

where \( \lambda \) labels the layers from 1 to \( n \) and \( z_\lambda \) is the corresponding perpendicular distance of the \( \lambda \) layer from the point \( \rho \) above the surface. The superscript labelling the field component indicates
the sign of the ion charge. The anion contributions $F_z^-, F_x^-$ and $F_y^-$ may be obtained from (3.49) and (3.50) by using the correct sign with $Q$ and transforming the $xy$ coordinates:

$$
\begin{align*}
    x'' &= x' + a/2 \\
    y'' &= y' + a/2
\end{align*}
$$

The last term in (3.48) is not carried through in the determination of $F_z$ since it will introduce a constant term containing $Q$. This will cancel on adding the cation and anion contributions. However the term must be included if the total field above a single ion array is required.

Equation (3.49) and (3.50) were tested by letting $n_n + \rightarrow \infty$ and determining the field for an ideal sodium chloride crystal. This was found to be in agreement with the calculation in §3.2.1. Further to this, the relaxed layer contribution to $\lambda$ was calculated using the layer positions of Benson, Freeman and Demsey (1963). The results from (3.49) and (3.50) were compared to a direct summation of the field contributions from $\approx 3 \times 10^5$ ions. This was found to be slowly converging and within less than 1% to the series answer.

3.3 CONTOUR PLOTTING ALGORITHM

It is useful to be able to present the potential energy field above the surface in the form of a contour diagram. Fig. 3.3 shows the $|F|$ electric field in such a form. Unfortunately the calculation of the total adsorption potential energy field is lengthy, even on the 1904A ICL machine. Since only a limited number of points within the unit cell can be generated, numerical methods are required to obtain the contour lines. The algorithm adopted here makes full use of the symmetry of the cubic unit cell. More general methods could have been developed but would not have been used in the present work.
A 12 × 12 grid was constructed with the cations at the vertices and the anion at the centre. The symmetry of the lattice was such that the field was conveniently represented by a set of one-dimensional Fourier curves with a period equal to the cation–cation distance.

The potential field, or whatever quantity above the surface required monitoring, was evaluated at 28 grid points (a grid point corresponds to the intersection of two grid lines). This area was equal to \( \frac{1}{4} \) of the total grid field and the number of evaluations was convenient for computational purposes. The Fourier curves were then determined from these points by a 12 point numerical fitting scheme (Kufner 1971).

The interpolating function was written:

\[
 f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left( a_n \cos(2\pi nx/a) + b_n \sin(2\pi nx/a) \right) \tag{3.52}
\]

where \( 'a' \) is the period and \( a_0, a_n, b_n \) the Fourier coefficients.

The first point along the grid line was labelled \((x_0, y_0)\) and the last \((x_{12}, y_{12})\) where \( f(x_0) = f(x_{12}) \). The coefficients \( a_n \) and \( b_n \) were obtained from:

\[
 a_n = \frac{2}{K} \left\{ y_0 + y_1 \cos\left(2\pi n/K\right) + y_2 \cos\left(4\pi n/K\right) + \ldots \right\} y_{K-1} \cos\left[\frac{2\pi n(K - 1)}{K}\right] \right\} \tag{3.53}
\]

\[
 b_n = \frac{2}{K} \left\{ y_1 \sin\left(2\pi n/K\right) + y_2 \sin\left(4\pi n/K\right) + \ldots \right\} y_{K-1} \sin\left[2\pi n(K - 1)\right] \right\} \tag{3.54}
\]

where \( K \) is the number of points (\( K = 12 \)) and \( n \) the label of the coefficients. For computational purposes, the Runge's scheme, for the calculation of \( a_n \) and \( b_n \), was found efficient (see Kufner 1971).
STEP A

\[
\begin{array}{cccccc}
\gamma_0 & \gamma_1 & \gamma_2 & \gamma_3 & \gamma_4 & \gamma_5 \\
\gamma_{11} & \gamma_{10} & \gamma_9 & \gamma_8 & \gamma_7 \\
\sum & u_0 & u_1 & u_2 & u_3 & u_4 & u_5 & u_6 \\
\text{Difference} & v_1 & v_2 & v_3 & v_4 & v_5 \\
\end{array}
\]

STEP B

\[
\begin{array}{cccc}
\upsilon_0 & \upsilon_1 & \upsilon_2 & \upsilon_3 & \upsilon_4 \\
\upsilon_5 & \upsilon_6 & \upsilon_7 & \upsilon_8 \\
\sum & s_0 & s_1 & s_2 & s_3 & \sum & \sigma_1 & \sigma_2 & \sigma_3 \\
\text{Difference} & d_0 & d_1 & d_2 & \text{Difference} & \delta_1 & \delta_2 \\
\end{array}
\]

The coefficients were obtained from:

\[
\begin{align*}
12a_0 &= s_0 + s_1 + s_2 + s_3 \\
6a_1 &= d_0 + 0.8660d_1 + 0.5d_2 \\
6a_2 &= (s_0 - s_3) + 0.5(s_1 - s_2) \\
6a_3 &= d_0 - d_2 \\
6b_1 &= 0.5\sigma_1 + 0.8660\sigma_2 + \sigma_3 \\
6b_2 &= 0.8660(\delta_1 + \delta_2) \\
6b_3 &= \sigma_1 - \sigma_3
\end{align*}
\]

Here \( n = 6 \) was found to be sufficient for convergence of the series to the required accuracy. The Fourier series were then used to "magnify" the grid by interpolating 4 new points between existing grid points. This was done in stages to give a new 61 x 61 grid, subsequently used for contour searching. The contour was constructed by a series of linear searches along one set of parallel grids.
grid points in the closest proximity to the contour value were then used in a Lagrangian interpolation routine, (ICL SRF7 library, routine F4LACRNG), to obtain the full coordinates of the required contour value. The whole length of each grid was searched so that multiple contour intersections on individual grid lines could be located and stored in separate locations. These stored coordinates for individual contour lines were subsequently output to the Loughborough University graph plotting routines, UTP4A and UTP4B.

3.4 THE HINDERED TRANSLATION MODEL

As mentioned in §3.1, the state of the adsorbate may be investigated when the potential field above the surface is known. In the limiting case of an isolated atom adsorbed on the surface, the problem of determining the adsorbate state may conveniently be solved by using the hindered translation (ht) model after Hill (1946). He originally used the model to determine the heat capacity of the adsorbate's xy motion as a function of temperature. Unfortunately no reliable parameters were available for this evaluation on a specific system and so only general conclusions could be drawn. The treatment is further developed here to calculate the internal energy associated with the xy motion, \( a \Delta E_{xy} \), which is used in the calculation of the isosteric enthalpy of adsorption (§3.5.4).

The assumptions implicit in the ht model are first summarized:

(i) The surface consists of a square lattice of adsorption sites with a nearest neighbour distance such that:

\[
A = M(a')^2
\]

where \( M \) is the number of sites, \( A \) is the surface area and \( a' \) the periodicity of the adsorption sites.

(ii) The number of adsorbed atoms, \( n_a \ll M \).
(iii) The $xy$ motion of the adsorbed atom is assumed independent of the $z$ motion.

(iv) The $z$ motion is taken as vibrational, being represented by a one-dimensional harmonic partition function.

(v) The minimum adsorption potential energy field above the surface may be represented by a double cosine formula:

$$U^0(x,y) = U_{00} + \frac{1}{2}V_{\text{max}}(1 - \cos 2\pi x/a') + \frac{1}{2}V_{\text{max}}(1 - \cos 2\pi x/a')$$  

(3.56)

where $U_{00}$ is the overall minimum in the potential field over the cell, and $V_{\text{max}}$ is the maximum energy barrier to translation across the surface. In the case of sodium chloride and potassium chloride $a' = a$.

The system partition function may then be written:

$$Q = \frac{1}{n_a!} \frac{M!}{(M-n_a)!} [f(T)]^{n_a}$$  

(3.57)

where the subsystem partition function is:

$$f(T) = f_{xy} f_z \exp(-U_{00}/kT)$$  

(3.58)

From (ii)

$$Q = \frac{1}{n_a!}[f(T)]^{n_a}$$  

(3.59)

In the limit of a very dilute adsorbed gas, the $xy$ contribution to the adsorbed atom partition function may be written (Pitzer and Gwinn 1942):

$$f_{xy} = f_{\text{class}} \times f_{\text{ho-q}} / f_{\text{ho-c}}$$  

(3.60)

where $f_{\text{class}}$ is the classical value of $f_{xy}$, $f_{\text{ho-q}}$ is the quantum oscillator partition function for the motion about the minimum in the $xy$ adsorption potential field, $U_{00}$, and $f_{\text{ho-c}}$ is the classical
limit of \( f_{\text{ho-q}} \). Equation (3.60) has the correct asymptotic behaviour:

\[
\begin{align*}
\text{Lim}_{T \to \infty} f_{\text{ho-q}} &= f_{\text{ho-c}} \\
\Rightarrow f_{xy} &= f_{\text{class}} \\
\text{Lim}_{T \to 0} f_{\text{class}} &= f_{\text{ho-c}} \\
\Rightarrow f_{xy} &= f_{\text{ho-q}}
\end{align*}
\]

\[ (3.61) \]

\[ (3.62) \]

\( f_{\text{class}} \) is obtained from the configurational integral using \((U^0 - U_{00})\) from (3.56), yielding:

\[
f_{\text{class}} = \frac{2\pi mkT}{\hbar^2} A^2_0(u) \exp(-2u)
\]

\[ (3.63) \]

where \( u = \sqrt{\text{max}}/4kT \) and \( I_0(u) \) is a modified Bessel function of the first kind of zero order.

\( f_{\text{ho-c}} \) is obtained from:

\[
\text{Lim}_{u \to \infty} f_{\text{class}} = m(kT/\hbar)^2
\]

\[ (3.64) \]

since

\[
\text{Lim}_{u \to \infty} I_0(u) = \exp(u)/(2\pi u)^\frac{3}{2}
\]

and

\[
v_x = v_y = v' = \left[ \frac{\text{max}}{\hbar ma^2} \right]^{\frac{1}{2}}
\]

where \( v_x \) and \( v_y \) are the x and y components of the atomic vibrational frequencies.

The classical expression for the one-dimensional partition function is:

\[
f_{1D} = \exp(-\hbar v/2kT)/[1 - \exp(-\hbar v/kT)]
\]

\[ (3.65) \]

\[
\text{Lim}_{T \gg \hbar v/k} f_{1D} = \frac{kT}{\hbar v}
\]

\[ (3.66) \]
A comparison of (3.66) with (3.64) leads to $f_{ho-q}$:

$$f_{ho-q} = M \left[ \frac{\exp(-h \nu'/2kT)}{1 - \exp(-h \nu'/kT)} \right]^2$$  \hspace{1cm} (3.67)

Using these expressions, (3.60) becomes:

$$f_{xy} = 2 \pi w \Pi_0^2(u) \exp(-2u) \left\{ \frac{\exp(-Wu)}{1 - \exp(-Wu)} \right\}^2$$  \hspace{1cm} (3.68)

where

$$W = \left( \frac{4h^2}{m a W_{\text{max}}} \right)^\frac{1}{2}$$  \hspace{1cm} (3.69)

These are the same equations as given previously by House and Jaycock (1974b) but with $V$ replacing $V_{\text{max}}/2$.

The $xy$ internal energy and specific heat contributions to the adsorbed phase may be obtained by the usual methods:

$$aE^{xy} = kT^2 \left( \frac{\partial^2 n_{xy}}{\partial T} \right) A_n a$$  \hspace{1cm} (3.69)

$$c^{xy}_s = \left( \frac{\varepsilon_{xy}}{T} \right) A_n a$$  \hspace{1cm} (3.70)

Since

$$I_0'(u) = I_1(u)$$

and

$$\frac{d(uI_1(u))}{du} = uI_0'(u)$$

where $I_1(u)$ is a first order modified Bessel function

$$aE^{xy} = kT \left\{ -1 - 2uI_1(u)/I_0(u) + Wu + 2u + 2Wu \exp(-Wu)/[1 - \exp(-Wu)] \right\}$$  \hspace{1cm} (3.71)
The isotherm equation may be obtained by equating the chemical potentials of the bulk gas and the adsorbed phase. For the adsorbed phase:

\[ a^\mu = -kT \left( \frac{2^n}{\delta n} \right) A, T \]  

(3.73)

This may be evaluated by using Stirling's approximation, (Knuth 1966), and the expressions for \( f_{xy} \) and \( f_z \). Using (3.58) and (3.59), the equilibrium condition gives:

\[ \frac{n_a}{A} = K_H \times P \]  

(3.74)

where \( P \) is the bulk gas pressure and \( K_H \) is the Henry's law constant given by:

\[ K_H = 2\pi u \exp(-2u)I_0^2(u)f_z \exp(U_0/kT)\exp(\mu^0(T)/kT) \exp(-W_u)/a^2[1 - \exp(-W_u)]^2 \]  

(3.75)

where \( \mu^0 \) is the standard chemical potential of the bulk gas.

These equations will be used in the analysis of the results from the single gas atom-surface interaction, discussed in §3.5 and §3.6, and also compared to the gas-solid virial calculation (Chapter 4).

3.5 COMPUTATION USING THE FROST AND WOODSON APPROXIMATION

3.5.1 Introduction

The FW approximation was discussed in §2.8. The inert gas core self-interaction and mixed interaction parameters for the "exp6" function were taken from Mason (1955). These are not the most reliable but are the only consistent set available for all the gases.
studied here i.e. helium, neon, argon, krypton and xenon. The calculations of the adsorption energy potential field are for these gases on the ideal (100) face of sodium chloride. A comparison with argon on the (100) potassium chloride surface is also made. Sodium chloride is chosen as the principle adsorbent since it may be easily prepared experimentally in the simple cubic form with largely only the (100) plane exposed. In the case of potassium chloride, the analysis of the experimental results is more difficult since the (100) and (111) faces are usually present.

3.5.2 Determination of the Potential Energy Minimum

Within the additive approximation the total interaction energy between a gas atom and a solid, $U_s(x)$, may be expressed in terms of sums over the ions of the single attractive and repulsive interactions, $U^{\text{dis}}$ and $U^{\text{rep}}$, plus the total electrostatic interaction, $U^e$.

To calculate the $U^{\text{dis}}$ and $U^{\text{rep}}$ sums, the origin of the coordinate system was chosen so that the cations in the surface occupied the positions given by $(n d, m d, 0)$ where $n$ and $m$ are real integers and $d$ the lattice period defined by $d = a/2^{1/2}$, where $a$ is the usual cation-cation distance along the $x$ axis in fig. 3.1. It follows that the surface anions occupied the positions $[(n + \frac{1}{2})d, (m + \frac{1}{2})d, 0]$. The procedure for obtaining the potential energy minimum, $U^0$, was programmed in Fortran IVD and consisted of the following stages:

(i) The potential energy was calculated numerically at a series of distances corresponding to the bringing of the inert gas atom towards the surface in the $-z$ direction. A direct summation over a hemispherical region of the semi-infinite crystal extended so as to include 3000 ions, the contribution due to ions outside this region was sufficiently small to be neglected. In certain circumstances it proved possible to curtail the summa-
tion of the repulsive term because of rapid convergence so that a smaller number of ions were considered for this term.

(ii) The electrostatic contribution to the total energy, $U^e$, was evaluated at each position using the Fourier method described in §3.2.1.

(iii) The total potential energy, $U_s(r)$, was calculated for each distance from the surface until such a point that $U_s(r)$ began to increase. A quartic polynomial was then fitted through the points $(U_s(r), z)$ using a least-squares technique and the minimum of the function found numerically using the Newton-Raphson method. This method, (see Hildebrand 1956), does not always converge. In general, if the function exhibits turning points or inflections between the initial estimate of the solution and the true solution, the iterations may not converge to the correct root. The conditions for convergence are dealt with in some detail by Hildebrand (1956). This problem of convergence was met in using the quartic fit. However, it could generally be overcome by choosing different starting points to obtain the iterative solution. However, because of this problem, the program was later modified, as explained in §3.6.3.

(iv) The initial estimate of the potential minimum was then used to define a region for the calculation of a second series of values of $(U_s(r), z)$ which were then fitted by a least-squares method to a parabola. This last step was repeated with six points at distances separated by 0.001 nm. to accurately fix the minimum values of $U_s(r)$ and the corresponding $z$, which will be termed $U^0$ and $z^0$ respectively.
3.5.3 The Values of \( U^0 \) and \( z^0 \)

The adsorption energy contour maps are shown in fig. 3.4. Table 3.1 gives the values of \( U^0 \) at three different positions over the lattice together with the equilibrium distance from the surface, \( z^0 \), and the minimum barrier to translation on the surface, \( V^0 \).

**TABLE 3.1** VALUES OF \( U^0 \), \( z^0 \) AND \( V^0 \) AT THREE DIFFERENT POSITIONS ON THE SURFACE

Position (a) over a cation; (b) over anion and (c) over the centre of the unit cell.

<table>
<thead>
<tr>
<th>System</th>
<th>( U^0 / \text{kJmol}^{-1} )</th>
<th>( z^0 / \text{nm} )</th>
<th>( V^0 / \text{kJmol}^{-1} )</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/NaCl</td>
<td>2.118</td>
<td>0.230</td>
<td>1.034</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>0.774</td>
<td>0.237</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>1.084</td>
<td>0.274</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Ne/NaCl</td>
<td>3.132</td>
<td>0.269</td>
<td>0.448</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>1.813</td>
<td>0.325</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2.684</td>
<td>0.267</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Ar/NaCl</td>
<td>7.183</td>
<td>0.292</td>
<td>1.783</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>3.910</td>
<td>0.359</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>5.400</td>
<td>0.312</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Kr/NaCl</td>
<td>10.05</td>
<td>0.283</td>
<td>3.32</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>5.02</td>
<td>0.362</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>6.73</td>
<td>0.318</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Xe/NaCl</td>
<td>12.73</td>
<td>0.300</td>
<td>3.81</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>6.76</td>
<td>0.376</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>8.92</td>
<td>0.334</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Ar/KCl</td>
<td>5.061</td>
<td>0.351</td>
<td>0.532</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>5.061</td>
<td>0.351</td>
<td></td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>6.476</td>
<td>0.309</td>
<td></td>
<td>c</td>
</tr>
</tbody>
</table>

The symmetry of the field is generally the same for all the inert gases on sodium chloride. In the case of neon on sodium...
Fig. 3.4  Isopotential energy curves, values shown in kJ mol\(^{-1}\), for the interaction of, (a) He (b) Ne (c) Ar (d) Kr and (e) Xe, with the (100) NaCl face and (f) for the interaction of Ar with the (100) face of KCl

Key: 
- cation
- anion
Fig. 3.5

Variation of the minimum adsorption potential energy about the Na\(^+\) position along the line \(y' = 0\), for the inert gases using the coordinate system shown in fig. 3.1. The ordinate axis gives the fractional change in the minimum relative to the \(U^0(0,0,z^0)\) value. \([\Delta U^0 = U^0(0,0,z^0) - U^0(x'0,z^0)]\); \(d\) is the period along the \(x'\) line.
chloride, a small annular well exists in the vicinity of the sodium ion. This is shown in fig. 3.5. With argon on potassium chloride the minimum in the field is at the midcell position. Although helium on sodium chloride has a higher translational barrier than neon, the barrier increases throughout the remainder of the series.

3.5.4 The Calculation of the Isosteric Enthalpy at Zero Coverage

The values of $U^0$ that have been calculated are not directly comparable with experimentally determinable parameters, the most convenient of which being the isosteric enthalpy of adsorption, $q_{st}$. (This is sometimes called the isosteric heat.) The isosteric (constant surface coverage) enthalpy for adsorption from an ideal bulk gas may be conveniently expressed (see Hill 1952):

$$q_{st} = \frac{\phi_H}{g} - \frac{\phi_h}{a}$$

(3.76a)

where the tildes $\tilde{}$ and $\overline{}$ refer to the mean and partial molar quantities and the subscripts 'g' and 'a' to the bulk gas and adsorbed phase.

The isosteric enthalpy is related to the differential energy of adsorption, $q_{diff}$, by:

$$q_{st} = q_{diff} + RT$$

(3.76b)

To evaluate $q_{diff}$, a model describing the adsorption state is required. It is usually convenient to use either of the following assumptions:

(i) That the Hill-de Boer model (§5.2.1 equation 5.11) is applicable in which the kinetic energy change on adsorption, $\Delta E^{kin} = -\frac{1}{2}RT$.

The vibrational energy of the adsorbed atoms at temperature $T$,
E_{\text{Vib}}^a$, is due only to vibrational motion normal to the surface. (ii) That the localized Langmuir or Fowler-Guggenheim models (§5.2.2 and 5.2.3) are valid, for which $E^{\text{kin}} = -\frac{3}{2}RT$ and the energy of vibration may be obtained from a consideration of 3-dimensional vibration in a potential well.

For case (i)

$$\lim_{q \to 0} q_{\text{diff}}^{\text{st}}(m) = U^0 - E_{\text{Vib}}^a - \Delta E$$

(3.77)

where (m) denotes the mobile model. Thus:

$$q_{\text{st}}^{\text{st}}(m) = U^0 - E_{\text{Vib}}^a + \frac{3}{2}RT$$

(3.78)

For case (ii)

$$q_{\text{st}}^{\text{st}}(l) = U^0 - E_{\text{Vib}}^a + \frac{5}{2}RT$$

(3.79)

where (l) denotes the localized model.

The z-component of the vibrational frequency, $v^z$, may be determined directly from the "best fit" parabola for $U_s(r)$ around $U^0$ and making the simple harmonic approximation:

$$f_z = \left[\frac{\partial^2 U_s(r)}{\partial z^2}\right]_{x,y,z=0}$$

(3.80)

giving

$$v^z = \frac{1}{2\pi}(f_z/m)^\frac{1}{2}$$

(3.81)

where $f_z$ is the force constant and $m$ the mass of the adsorbed atom. Similar expressions are available for $v_x$, $v_y$, the x and y direction vibrational frequencies. In the latter cases $U^0(x,y,z)$ may be obtained in the form of a Fourier curve, which for the case of $f_x$ gives

$$f_x = -\frac{6}{n=1}a_n(2\pi)^2 \frac{z^2}{a^2} \cos\left(\frac{2\pi n x}{a}\right)$$

(3.82)
TABLE 3.2 ISOSTERIC ENTHALPY (77.5K) AT ZERO COVERAGE USING MOBILE AND LOCALIZED MODELS. EXPERIMENTAL VALUES OF $q_{st}^*$ (76K) ARE TAKEN FROM (a) HAYAKAWA (1957b) AND (b) ROSS AND HINCHEN (1970)

<table>
<thead>
<tr>
<th>System</th>
<th>$\nu^*/10^{12} \text{s}^{-1}$</th>
<th>$E^*/\text{kJmol}^{-1}$</th>
<th>$q_{st}^{(m)}/\text{kJmol}^{-1}$</th>
<th>$\nu''/10^{12} \text{s}^{-1}$</th>
<th>$E''/\text{kJmol}^{-1}$</th>
<th>$q_{st}^{(l)}/\text{kJmol}^{-1}$</th>
<th>Expt. $q_{st}^*/\text{kJmol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/NaCl</td>
<td>2.740</td>
<td>0.791</td>
<td>2.293</td>
<td>1.57</td>
<td>1.388</td>
<td>1.549</td>
<td>-</td>
</tr>
<tr>
<td>Ne/NaCl</td>
<td>1.489</td>
<td>0.689</td>
<td>3.410</td>
<td>0.70</td>
<td>1.309</td>
<td>2.746</td>
<td>-</td>
</tr>
<tr>
<td>Ar/NaCl</td>
<td>1.418</td>
<td>0.685</td>
<td>7.464</td>
<td>0.55</td>
<td>1.301</td>
<td>6.808</td>
<td>9.17 (a)</td>
</tr>
<tr>
<td>Kr/NaCl</td>
<td>1.061</td>
<td>0.667</td>
<td>10.35</td>
<td>0.44</td>
<td>1.297</td>
<td>9.700</td>
<td>6.86 (b)</td>
</tr>
<tr>
<td>Xe/NaCl</td>
<td>0.876</td>
<td>0.660</td>
<td>13.03</td>
<td>0.37</td>
<td>1.294</td>
<td>12.39</td>
<td>-</td>
</tr>
<tr>
<td>Ar/KCl</td>
<td>1.092</td>
<td>0.668</td>
<td>6.773</td>
<td>0.70</td>
<td>1.309</td>
<td>6.11</td>
<td>8.71 (a)</td>
</tr>
</tbody>
</table>
where $a_n$ are the Fourier coefficients of (3.53), $d$ the period and $x_0^0, y_0^0$ the $xy$ coordinates of the minimum in the $xy$ potential field. For the cubic system at the cation and anion positions $v_x = v_y = v''$. These frequencies may be used to calculate the vibrational contribution to the internal energy of the adsorbed phase. The molar vibrational energy for one degree of vibrational freedom may be expressed as

$$a_E^{\text{vib}} = \frac{Lh\nu}{2} + \frac{Lh\nu \exp(-h\nu/kT)}{[1 - \exp(-h\nu/kT)]}$$

(3.83)

from which $a_E^\perp$ and $a_E^\parallel$, the respective vibrational energies perpendicular and parallel to the surface, may be calculated. The results of these calculations are shown in Table 3.2.

Hayakawa's (1957b) isosteric enthalpies are greater than expected, but the results of Ross and Hinchen (1970) indicate values in agreement with this calculation. As discussed in §6.3.1, Hayakawa's samples were more heterogeneous than Ross and Hinchen's, resulting in linear extrapolation to higher $a_{st}$ values.

An interesting feature concerning these calculations over 196 positions above the unit cell is that $a_E^\perp$ does not vary by more than $30 J \text{ mol}^{-1}$ over the entire surface in all cases except helium on sodium chloride. Selected values are shown in Table 3.3.

<table>
<thead>
<tr>
<th>TABLE 3.3 VARIATIONS OF $a_E^\perp / \text{kJ mol}^{-1}$ WITH POSITION ON THE SURFACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site positions as described in Table 3.2.</td>
</tr>
<tr>
<td>system</td>
</tr>
<tr>
<td>position</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
</tbody>
</table>
3.5.5 Application of the Hindered Translation (ht) Model

A preliminary estimate of the state of an adsorbed atom may be obtained by consideration of the quantum energy states of a one-dimensional oscillator located at the potential energy minimum. The fraction of oscillators with energy $E_{\text{vib}}$ greater than or equal to $(n + \frac{1}{2})\hbar \omega$ is given by $\exp(-nh\omega/kT)$ (Rushbrooke 1967). The smallest value of $n$ satisfying the condition:

$$\frac{(n + \frac{1}{2})\hbar \omega}{kT} \geq E_{\text{vib}}$$

may be used to determine the ratio $R_a$ of adsorbed atoms translating, ($u^0 > E_{\text{vib}} > v^0$), to those non-translating, ($E_{\text{vib}} < v^0$), which is given by:

$$R_a = \frac{\exp(-n_1 h\omega/kT) - \exp(-n_2 h\omega/kT)}{1 - \exp(-n_1 h\omega/kT)}$$

(3.85)

where $n_1$ and $n_2$ are given by (3.84) with $E_{\text{vib}}$ equal to $v^0$ and $u^0$ respectively. The classical equation analogous to (3.85) is a poor approximation in this case. Table 3.4 gives $R_a$ values at a series of temperatures for the inert gas-sodium chloride system. The table suggest a considerable degree of localization exists for the adsorption of argon, krypton, and xenon on sodium chloride at low temperatures.

A similar result is obtained if the (ht) model is used to determine the isosteric enthalpies.

$$q_{0}^{st}(ht) = \frac{c_{pT}}{2} - \left[ E_{a}^{\text{XY}} + E_{a}^{\perp} - u_{0}(x^0, y^0, z^0) \right]$$

(3.86)
TABLE 3.4 VALUES OF THE RATIO, $R_a$, OF ATOMS TRANSLATING TO THOSE NON-TRANSLATING FOR THE ADSORPTION OF INERT GASES ON NaCl AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>gas</th>
<th>50</th>
<th>77.5</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.31</td>
<td>0.65</td>
<td>0.91</td>
<td>1.38</td>
</tr>
<tr>
<td>Ar</td>
<td>0.017</td>
<td>0.077</td>
<td>0.15</td>
<td>0.34</td>
</tr>
<tr>
<td>Kr</td>
<td>0.00028</td>
<td>0.0053</td>
<td>0.017</td>
<td>0.072</td>
</tr>
<tr>
<td>Xe</td>
<td>0.00012</td>
<td>0.0026</td>
<td>0.0099</td>
<td>0.048</td>
</tr>
</tbody>
</table>

$\alpha_{\text{E}_{\text{XY}}}^\text{st}$ may be obtained from (3.71) and $\alpha_{\text{E}}^\perp$ from Table (3.2). The resulting values of $q_{\text{O}_{\text{st}}}$ and $\alpha_{\text{E}_{\text{XY}}}$ are presented in Table 3.5.

TABLE 3.5 ISOSTERIC ENTHALPIES, $q_{\text{O}_{\text{st}}}(ht)$, AND THE INTERNAL ENERGY CONTRIBUTION, $\alpha_{\text{E}_{\text{XY}}}$, AT 77.5K USING THE HINDERED TRANSLATION MODEL

<table>
<thead>
<tr>
<th>system</th>
<th>$\alpha_{\text{E}_{\text{XY}}}^\text{st}/\text{kJ mol}^{-1}$</th>
<th>$q_{\text{O}_{\text{st}}}(ht)/\text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/NaCl</td>
<td>1.169</td>
<td>1.769</td>
</tr>
<tr>
<td>Ne/NaCl</td>
<td>1.146</td>
<td>2.896</td>
</tr>
<tr>
<td>Ar/NaCl</td>
<td>1.413</td>
<td>6.696</td>
</tr>
<tr>
<td>Kr/NaCl</td>
<td>1.429</td>
<td>9.570</td>
</tr>
<tr>
<td>Xe/NaCl</td>
<td>1.414</td>
<td>12.26</td>
</tr>
<tr>
<td>Ar/KCl</td>
<td>1.167</td>
<td>6.255</td>
</tr>
</tbody>
</table>

A comparison with Table 3.2 shows that in all cases $q_{\text{O}_{\text{st}}}(ht)$ is nearer $q_{\text{O}_{\text{st}}}(\perp)$ than $q_{\text{O}_{\text{st}}}(\parallel)$. 
Fig. 3.6 The $c_Y^X$ contribution to the heat capacity, $c_Y^X$, for the inert gases as a function of temperature.

Key:
- - - on NaCl
- - - - on KCl

The curves represent the heat capacity of the inert gases: Ne, Ar, Kr, Xe, and He, plotted against temperature ($T/K$).
The theoretical heat capacity curves for the \( \chi \) motion, (equation 3.72), shown in fig. 3.6, all exhibit well defined maximum and are asymptotic to \( C_\chi^V/T = 1.0 \) in the higher temperature region. At the present time no measurements are available for testing this theoretical prediction. Figure 3.6 also illustrates that xenon, krypton and argon on sodium chloride are all in the region of the beginning of the localized to mobile transition at 77.5K, but that argon on potassium chloride and helium and neon on sodium chloride at the same temperature show appreciable mobility.

3.6 COMPUTATION OF THE EFFECTS OF SURFACE RELAXATION USING MAYER’S DISPERSION CONSTANTS FOR THE IONS

3.6.1 Introduction

The calculation of the surface distortion of alkali halide crystals has been made by Benson, Freeman and Dempsey (1963). They have allowed relaxation of the ions in the first five layers, \( \lambda = 0 \) to \( \lambda = 4 \), of the crystal. Positive and negative ions of layer \( \lambda \), are assumed to be displaced from the regular lattice sites, in the direction of the outward normal to the surface, by distances \( z_\lambda^+a \) and \( z_\lambda^-a \) where 'a' is the nearest neighbour distance. The relaxed ions have dipole moments, \( \mu_\lambda^+ \) and \( \mu_\lambda^- \), in the same directions as the displacements. The interactions between the ions is assumed to consist of the Born-Mayer type repulsion and the usual dispersion attraction, plus charge-dipole and dipole-dipole interactions. Benson et al (1963) used the dispersion coefficients of Mayer (1933), electron polarizabilities of the ions from Tessman, Kahn and Shockley (1953) and the BM parameters from Cubicciotti (1959, 1960), to calculate the distortion energy. This is the difference in energy of the crystal in the relaxed and ideal states. Since there are \( 4n \) variables associated
with \( n \) layers of relaxed crystal, the problem is to determine the minimum in the distortion energy by an optimization procedure. This is achieved by calculating the first derivatives of the distortion energy with respect to \( z_A \), and then using a Newton-Raphson procedure to determine the variables (Benson et al 1963). The values of \( z_A^+ \) and \( z_A^- \) used here are shown in Table 3.6.

**TABLE 3.6** THE RELAXATION PARAMETERS IN REDUCED UNITS \( z_A^+ \) AND \( z_A^- \)

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>sodium chloride</th>
<th>potassium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z_A^+ )</td>
<td>( z_A^- )</td>
<td>( z_A^+ )</td>
</tr>
<tr>
<td>0</td>
<td>-0.08708</td>
<td>0.03558</td>
</tr>
<tr>
<td>1</td>
<td>0.12945</td>
<td>0.02160</td>
</tr>
<tr>
<td>2</td>
<td>-0.05502</td>
<td>0.01098</td>
</tr>
<tr>
<td>3</td>
<td>0.05409</td>
<td>0.00458</td>
</tr>
<tr>
<td>4</td>
<td>-0.02011</td>
<td>0.00106</td>
</tr>
</tbody>
</table>

Benson and Claxton (1968) repeated the calculations using the shell model for the ions. This model allows a relative displacement of the nucleus and electron centre of the ions. The analysis gave similar trends to the earlier work but the relaxation distances were smaller. Since the single charge model is consistent with the calculation of the electric field in §3.2, the earlier results are used here. Unfortunately it has not been possible to use low energy electron diffraction methods to provide experimental evidence of the amount of relaxation. The theoretical work does seem to indicate that the values in Table 3.6 are an upper limit to the solution of the relaxation problem.
3.6.2 The Gas-Ion Potential Parameters

The analysis is now restricted to argon and krypton adsorbed on sodium chloride and potassium chloride. The TP parameters (§2.5) used for the inert gas atoms are combined (§2.9) with the ion parameters of Mayer (1933) and Tosi and Fumi (1964). The reasons for this choice have been discussed in Chapter 2. The resulting 'exp6' equation for the inert gas-ion interaction is specified in Table 3.7.

<table>
<thead>
<tr>
<th>System</th>
<th>$\epsilon/k$</th>
<th>$r_m$/nm</th>
<th>$\alpha$/nm</th>
<th>$\sigma$/nm</th>
<th>$r_{max}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Na$^+$</td>
<td>10.450</td>
<td>0.4120</td>
<td>18.712</td>
<td>0.3743</td>
<td>0.0359</td>
</tr>
<tr>
<td>Ar-Cl$^-$</td>
<td>148.97</td>
<td>0.3735</td>
<td>16.961</td>
<td>0.3370</td>
<td>0.0441</td>
</tr>
<tr>
<td>Kr-Na$^+$</td>
<td>100.37</td>
<td>0.4432</td>
<td>17.898</td>
<td>0.4014</td>
<td>0.0444</td>
</tr>
<tr>
<td>Kr-Cl$^-$</td>
<td>149.15</td>
<td>0.3984</td>
<td>16.088</td>
<td>0.3581</td>
<td>0.0549</td>
</tr>
<tr>
<td>Ar-K$^+$</td>
<td>46.114</td>
<td>0.4003</td>
<td>17.804</td>
<td>0.3625</td>
<td>0.0407</td>
</tr>
<tr>
<td>Ar-Cl$^-$</td>
<td>152.72</td>
<td>0.3734</td>
<td>16.606</td>
<td>0.3364</td>
<td>0.0469</td>
</tr>
<tr>
<td>Kr-K$^+$</td>
<td>44.088</td>
<td>0.4307</td>
<td>16.989</td>
<td>0.3887</td>
<td>0.0506</td>
</tr>
<tr>
<td>Kr-Cl$^-$</td>
<td>150.57</td>
<td>0.3992</td>
<td>15.748</td>
<td>0.3583</td>
<td>0.0585</td>
</tr>
</tbody>
</table>

The small dispersion energy contributions used in the cation self-interaction potentials lead to $\sigma$ and $r_m$ values for the cation-inert gas interactions larger than those obtained from the corresponding anion interactions.

The values of $c_1$ and $c_2$ of the BM equation determined by Tosi and Fumi (1964) are strictly applicable only when both $C_6$ and $C_8$
contributions to $U_{\text{dis}}$ are included in the ion-ion potential. Since the parameters in Table 3.7 were determined by neglecting the $C_8$ term, an assessment must be made of the error incurred. This can be done by writing the inert gas self-interaction:

$$U(r) = -\frac{C_6}{r^6} - \frac{C_8}{r^8} + c_1 \exp(-c_2 r)$$  \hspace{1cm} (3.87)$$

The $C$ constant in (2.34) already contains some contribution from the dipole-quadrupole term.

The $c_1$ and $c_2$ constants in (3.87) were determined for argon and krypton by a least-squares fit to the potential function of TP using the Kingston (1964) $C_6$ values and Fontana's (1961) $C_8$ values in (3.87). The best values of $c_1$ and $c_2$ were determined using 100 division intervals of $c_1$ and $c_2$ and then an iterative method to find the best fit to the potential well ($r = 0.3 - 0.6$ nm). The determined values of $c_1$ and $c_2$ for the inert gases were then used, with the combination rules, to give the ion-inert gas potential in the form of (3.87). If the same assumptions are made in the derivation of the combination rule for the $C_8$ parameter as in the case of the $C_6$ rule from London's equation, the geometric combination rule also holds for the $C_8$ term.

3.6.3 The Calculation of $U_s(r)$ for the Relaxed (100) Surface

The total dispersion and repulsion energies were calculated as in §3.5.2. Account was taken of $z_A^+$ and $z_A^-$. The electrostatic energy, $U^e$, contribution from the relaxed five layers was determined using the equations given in §3.2.2. The contribution of the remaining crystal was found using (3.41) with the correct choice of $z$.

The problem with the Newton-Raphson evaluation of the potential energy minimum, $U^0$, was eliminated by using an iterative step method.
The steps in \( z \) were halved as the minimum was approached. Only the last 6 points calculated were stored and subsequently used to fit a least-squares parabola to the potential minimum region so as to determine \( v \). This method also helped to reduce machine time.

3.6.4 Values of \( U^0 \) and \( z^0 \)

The effects of omitting the \( C_8 \) term from the ion-ion potential function can be assessed by comparing the results of the calculation of \( U^0 \) using (3.87) to those results using the 'exp6' with parameters from Table 3.7. Table 3.8 shows the percentage differences of the \( U^0 \) and \( V^0 \) values determined as described above. The changes are small enough for the \( C_8 \) ion-ion term to be excluded from remaining calculations, particularly in view of the large uncertainty (\( \sim 50\% \)) in both the inert gas and ion \( C_8 \) values.

**TABLE 3.8** PERCENTAGE CHANGES IN \( U^0 (x^0,y^0,z^0) \) AND \( V^0 \) OBTAINED BY INCLUDING THE \( C_8 \) DISPERSION TERM IN THE INERT GAS-ION POTENTIAL ENERGY INTERACTION FUNCTION

<table>
<thead>
<tr>
<th>system quantity</th>
<th>Ar/NaCl</th>
<th>Kr/NaCl</th>
<th>Ar/KCl</th>
<th>Kr/KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U^0(x^0,y^0,z^0) ) /kJmol(^{-1})</td>
<td>4.3</td>
<td>4.6</td>
<td>3.1</td>
<td>4.8</td>
</tr>
<tr>
<td>( V^0 ) /kJmol(^{-1})</td>
<td>4.3</td>
<td>13.6</td>
<td>3.9</td>
<td>12.0</td>
</tr>
</tbody>
</table>

The values of \( U^0 \), \( z^0 \) and \( V^0 \) for the relaxed and unrelaxed surfaces are presented in Table 3.9 for chosen positions on the unit cell. Figures 3.7 and 3.8 show the isopotential energy contour maps for the relaxed and unrelaxed surfaces.
Fig. 3.7 Isopotential energy curves, values shown in units of kJmol$^{-1}$
(a) Ar on the unrelaxed (100) face of NaCl, (b) Ar on the relaxed (100) face of NaCl, (c) Kr on the unrelaxed (100) face of NaCl, (d) Kr on the relaxed (100) face of NaCl

Key:  
• Na$^+$  
○ Cl$^-$
Fig. 3.8 Isopotential energy curves, values shown in kJ mol$^{-1}$, for the interaction of (a) Ar on the unrelaxed (100) face of KCl (b) Ar on the relaxed (100) face of KCl, (c) Kr on the unrelaxed (100) face of KCl, (d) Kr on the relaxed (100) face of KCl.

Key:  
- $\text{K}^+$  
- $\text{Cl}^-$
Fig. 3.9 Position of $U^0(x',y',z')$ for Ar on the relaxed (100) face of NaCl along the line $y' = 0$ i.e. the line joining the midcell and cation points. The ordinate axis gives the fractional change in the minimum relative to the $U^0(0,0,z')$ value. $[\Delta U^0 = U^0(0,0,z') - U^0(x',0,z')]$; $d$ is the period along the line $x' = 0$ in fig. 3.1.
Table 3.9 Values of $u^0$ and $z^0$ at Three Positions on the Relaxed and Unrelaxed Surface

Position (a) over the cation, (b) over the anion and (c) over the centre of the unit cell. $V^0$ is the minimum barrier to translation between sites.

<table>
<thead>
<tr>
<th>system</th>
<th>$u^0$/kJmol$^{-1}$</th>
<th>$z^0$/nm</th>
<th>$V^0$/kJmol$^{-1}$</th>
<th>position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unrelaxed</td>
<td>relaxed</td>
<td>unrelaxed</td>
<td>relaxed</td>
</tr>
<tr>
<td>Ar/NaCl</td>
<td>3.351</td>
<td>4.641</td>
<td>0.342</td>
<td>0.312</td>
</tr>
<tr>
<td></td>
<td>3.264</td>
<td>3.144</td>
<td>0.360</td>
<td>0.371</td>
</tr>
<tr>
<td></td>
<td>4.248</td>
<td>4.464</td>
<td>0.317</td>
<td>0.320</td>
</tr>
<tr>
<td>Kr/NaCl</td>
<td>3.810</td>
<td>3.697</td>
<td>0.381</td>
<td>0.392</td>
</tr>
<tr>
<td></td>
<td>4.785</td>
<td>4.992</td>
<td>0.344</td>
<td>0.347</td>
</tr>
<tr>
<td></td>
<td>2.993</td>
<td>3.203</td>
<td>0.363</td>
<td>0.351</td>
</tr>
<tr>
<td>Ar/KCl</td>
<td>3.575</td>
<td>3.490</td>
<td>0.357</td>
<td>0.356</td>
</tr>
<tr>
<td></td>
<td>4.703</td>
<td>4.818</td>
<td>0.308</td>
<td>0.302</td>
</tr>
<tr>
<td></td>
<td>3.560</td>
<td>3.802</td>
<td>0.385</td>
<td>0.373</td>
</tr>
<tr>
<td>Kr/KCl</td>
<td>4.084</td>
<td>3.999</td>
<td>0.379</td>
<td>0.378</td>
</tr>
<tr>
<td></td>
<td>5.074</td>
<td>5.197</td>
<td>0.339</td>
<td>0.333</td>
</tr>
</tbody>
</table>

As expected, the values of $u^0$ are lower than those calculated by the PW approximation (Table 3.1) or those calculated by Hayakawa (1957a) using the KM equation. This is a direct result of Mayer's lower dispersion constants for the ions (see Table 2.4).
The effects of relaxation, as expected from the magnitude of the displacements shown in Table 3.6, are more severe for the gases on sodium chloride than on potassium chloride. In fact the difference between the relaxed and unrelaxed computation for potassium chloride is small enough to be ignored at the present level of knowledge of the $U_s(r)$ field. For sodium chloride the effect of relaxation is much larger, showing about a 30% increase in $U^0$ at the cation position. A comparison of figs 3.7a, 3.7b and figs 3.7c, 3.7d shows the effects of relaxation in altering the position of $U^0(x^0, y^0, z^0)$. In the case of krypton on sodium chloride, the potential minimum in the field moves from the midcell position to the cation position after relaxation. For argon on sodium chloride, the effects of relaxation are less, the $U^0(x^0, y^0, z^0)$ position on the relaxed surface lying along the midcell to cation line as shown in fig. 3.9.

3.6.5 Application of the Hindered Translation Model

The isosteric enthalpy, $q^{st}(ht)$, may be calculated from (3.86) using the values of $E^1$ and $E^{XY}$ given in Table 3.10. The effects of the translational barrier are still evident if the $q^{st}(ht)$ results are compared to the $q^{st}(m)$ values (Table 3.10). The values of $q^{st}(ht)$ differ from the experimental results of Ross and Hinchen (1970) by about 30%. This indicates that the Mayer (1933) dispersion constants lead to a lower limit to the potential. This is because, using the Mayer constants, no value of $V^{\text{max}}$ could by itself increase $q^{st}$ by 30%. As indicated in Table 3.2, the differences, $q^{st}(m) - q^{st}(s)$, are in the range 0.75 - 0.65 kJ mol$^{-1}$ for all the systems studied.

The $C^{XY}_V$ values from (3.72) are shown in fig. 3.10. The localized to mobile transition occurs in the region of 20K and so at 77.5K, appreciable mobility of the adsorbate is expected for all the systems shown. The increased degree of localization on relaxing the crystal
Fig. 3.10 The $xy$ contribution to the heat capacity, $c^x_y$, as a function of temperature.

Key:
- $\cdots$ relaxed KCl
- $\cdots$ ideal NaCl
- $\cdots$ relaxed NaCl
surface is evident for argon and krypton on sodium chloride. The changes for argon and krypton on potassium chloride are much smaller and are not shown.

### TABLE 3.10 ISOSTERIC ENTHALPIES (77.5K) AT ZERO COVERAGE, CALCULATED USING THE ht MODEL AND THE MOBILE MODEL WITH RELAXED SURFACES

<table>
<thead>
<tr>
<th>system</th>
<th>$v_\perp$ /10^12 s^-1</th>
<th>$a^\perp$ /kJmol^-1</th>
<th>$a^{XY}$ /kJmol^-1</th>
<th>$q_0^{st}(ht)$ /kJmol^-1</th>
<th>$q_0^{st}(m)$ /kJmol^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/NaCl</td>
<td>1.108</td>
<td>0.665</td>
<td>1.187</td>
<td>4.480</td>
<td>5.018</td>
</tr>
<tr>
<td>Kr/NaCl</td>
<td>0.750</td>
<td>0.654</td>
<td>1.240</td>
<td>5.166</td>
<td>5.760</td>
</tr>
<tr>
<td>Ar/KCl</td>
<td>1.004</td>
<td>0.664</td>
<td>1.215</td>
<td>4.550</td>
<td>5.120</td>
</tr>
<tr>
<td>Kr/KCl</td>
<td>0.681</td>
<td>0.653</td>
<td>1.162</td>
<td>4.993</td>
<td>5.510</td>
</tr>
</tbody>
</table>

Finally the $K_H$ values may be calculated from (3.75). These values are compared to those from the mobile and localized models in Table 3.11.

### TABLE 3.11 VALUES OF THE HENRY'S LAW CONSTANT, $K_H/10^{13}$ atom N^-1, FOR ADSORPTION ON RELAXED SURFACES

<table>
<thead>
<tr>
<th>system</th>
<th>model</th>
<th>Ar/NaCl</th>
<th>Kr/NaCl</th>
<th>Ar/KCl</th>
<th>Kr/KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ht</td>
<td></td>
<td>2.05</td>
<td>6.56</td>
<td>2.85</td>
<td>5.95</td>
</tr>
<tr>
<td>2D</td>
<td></td>
<td>5.57</td>
<td>20.43</td>
<td>8.26</td>
<td>15.93</td>
</tr>
<tr>
<td>loc</td>
<td></td>
<td>1.55</td>
<td>4.78</td>
<td>2.09</td>
<td>4.47</td>
</tr>
</tbody>
</table>

The values of $K_H(ht)$ may be compared to those values of $K_H$ ob-
tained in Chapter 4. In this way, an assessment can be made of the reliability of the ht model.
4.1 INTRODUCTION

A series expansion of the form given in equation (2.37) was proposed by Thiesen (1885) to describe the state of an imperfect gas. The virial coefficients $B$, $C$, $D$, ... depend on the temperature and on the gas under consideration. The advantage of the virial equation over the other empirical equations of state of imperfect gases is that it may also be derived from a statistical thermodynamic study. The theoretical foundations of the virial equation of state are well understood both in the classical and quantum limits (Mason and Spurling 1969). It seems reasonable therefore that a similar virial expansion should be able to describe the state of a gas in the presence of a surface potential field. This method has been proposed by a number of researchers including Freeman and Halsey (1955), Everett (1965), Rudzinski, Waksmanzki, Suprynowicz and Rayss (1972), Morrison and Ross (1973), Steele (1973a, 1973b). The majority of the work has been concerned with its application to the inert gases on carbon blacks.

The purpose of the present work is to elucidate the effects of an ionic solid's periodic potential field on the calculation of the second two-dimensional virial coefficient. The system chosen is that of argon adsorbed on ideal and relaxed (100) sodium chloride. The Henry's law constant and isosteric enthalpy are also calculated by using the double Fourier expansion of the adsorption potential field that is developed here. This expansion, originally suggested by Steele (1973b) for the inert gas crystals, simplifies the problems of
determining the configurational integrals occurring in the expression for the two-dimensional virial coefficient. The method has been further developed here for ionic solids using the "exp6" interatomic potential function for the gas-ion interaction.

4.2 THE GAS-SOLID VIRIAL COEFFICIENTS

A complete development of the gas-solid virial equation will not be presented here because it can be found elsewhere (Steele 1967). However some ambiguities exist in the literature which require clarification. The model used here is based on the following assumptions:

(i) The adsorbent is an inert solid and further relaxation of the solid when the adsorbed atom approaches the surface is not allowed for. This is the same assumption as made in Chapter 3.

(ii) The interaction energies of the atoms in the gas are pairwise additive. The $U_s(r)$ field is determined using the same model as in Chapter 3.

(iii) Changes in the atomic substructure, i.e. nuclear or electronic, on adsorption are neglected.

(iv) The atoms obey classical statistical mechanics. This assumption is not restrictive since quantum effects in physical adsorption are negligible except for helium and hydrogen.

The total potential energy of $n$ atoms, in a configuration specified by the vectors $r_1, ..., r_n$, interacting with each other and with the adsorbent may be written:

$$U^*(r_1, ..., r_n) = \sum_{i=1}^{n} U_s(r_i) + \sum_{1 \leq i < j \leq n} U(r_{ij}) \tag{4.1}$$

where $U(r_{ij})$ are the gas self-interaction energies.

Using the independent variables, volume $V$, temperature, $T$, and chemical potential, $\mu$, the grand partition function, $Z$, can auto-
matically be written as a sum over one body, two body, three body,...
terms.
\[ z = \sum_{n=0}^{\infty} \frac{Z_n \lambda^n}{n!} \] (4.2)

where the activity of the gas is given by:
\[ \lambda = \exp(\mu/kT)/\Lambda^3 \] (4.3)

where for a monatomic gas
\[ \Lambda = \frac{h}{(2\pi m kT)^{\frac{3}{2}}} \] (4.4)

In fact the activity \( \lambda \) is related to the fugacity of the gas, \( f \), by
\[ \lambda = \frac{f}{kT} \] and fulfills the condition \( \lim_{\rho \to 0} \rho = \rho \)
\[ Z_n \] is the configurational integral:
\[ Z_n = \int \ldots \int_{V} S(r_1 \ldots r_n) dr_1 \ldots dr_n \] (4.5)

where \( S(r_1 \ldots r_n) \) is the generalized Boltzmann factor (classical case) or Slater sum (quantum case). In the classical limit
\[ Z_n = \int \ldots \int_{V} \exp \left[ \frac{U(r_1 \ldots r_n)}{kT} \right] dr_1 \ldots dr_n \] (4.6)

At equilibrium the chemical potential of the gas is the same throughout the system and for the bulk phase gas, (i.e. gas far from the surface), this becomes:
\[ \mu = kT \ln \left( \frac{PA^3}{kT} \right) \] (4.7)

Equation (4.7) is for an ideal gas. in this limit the activity becomes:
\[ \lambda = \frac{P}{kT} \] (4.8)
From the usual relationships, (Hill 1960), various properties of the system can be calculated e.g.

\[ n = kT \left( \frac{\partial \ln \Xi}{\partial n} \right)_{V,T} = \left( \frac{3\ln \Xi}{\partial \ln f} \right)_{V,T} \]  

(4.9)

In this model the concept of an adsorbed phase becomes less distinct. This is in contrast to the earlier description of the HT model (§3.4), when characteristic thermodynamic quantities were associated with a two-dimensional adsorbed phase. The number of atoms adsorbed, \( n_a \), is determined here by comparing the number present with the solid and then without, i.e.

\[ n_a = n - n_0 \]  

(4.10)

This corresponds to the Gibbs definition of surface excess (see Adamson 1967). The corresponding partition function for the system without the solid is:

\[ \Xi_0 = \exp(\Xi V) \]  

(4.11)

Equation (4.11) is applicable to an ideal gas. Using \( \Xi \) and \( \Xi_0 \) it is now possible to determine quantities associated with the surface excess of adsorbed atoms:

\[ n_a = \left( \frac{\partial \Xi^*}{\partial \ln \Xi} \right)_{T,V} \]  

(4.12)

\[ \Xi^* = \Xi/\Xi_0 \]  

(4.13)

where \( \Xi^* = E/\Xi_0 \)  

(4.14)

Steele (1967) has correctly shown that

\[ \Xi^* = \sum_{n=0}^{\infty} \frac{\Xi^*}{n!} \left( \frac{\partial \Xi^*}{\partial \ln f} \right)^n \]  

(4.15)
where
\[
\begin{align*}
Z_s^f &= Z_1 - V \\
Z_s^2 &= Z_2 - 2Z_1V + V^2
\end{align*}
\] (4.16a)

or in general:
\[
\begin{align*}
Z_s^n &= \sum_{R=0}^{n} (-1)^R \frac{n!}{R!(n-R)!} Z_{n-R}Z^n_0
\end{align*}
\] (4.16b)

where 
\[
Z^n_0 = V^n
\]

Now (4.12) may be evaluated by taking the series expansion of \( \ln Z^n_0 \)
and substituting for \( Z_s^n \) using (4.16), to give:
\[
\begin{align*}
n_a &= \frac{P}{kT}(Z_1 - V) + \left( \frac{P}{kT} \right)^2 (Z_2 - Z_1^2) \\
&\quad + \frac{Z_3 - 3Z_2Z_1 + 2Z_1^3}{2} \left( \frac{P}{kT} \right)^3
\end{align*}
\] (4.17a)

which may be rewritten in the form:
\[
\begin{align*}
n_a &= B_{AS} \left( \frac{P}{kT} \right) + C_{AAS} \left( \frac{P}{kT} \right)^2 + D_{AAS} \left( \frac{P}{kT} \right)^3 + \ldots
\end{align*}
\] (4.17b)

where the gas-solid virial coefficients are
\[
\begin{align*}
B_{AS} &= \int \{ \exp[-U_s(r_1)/kT] - 1 \} r_1 dr_1
\end{align*}
\] (4.18)

\[
\begin{align*}
C_{AAS} &= \int \int \{ \exp[-(U_s(r_1) + U_s(r_2)/kT)] r_{12} \} \, dr_1 \, dr_2
\end{align*}
\] (4.19)

\[
\begin{align*}
D_{AAS} &= \int \int \int \{ \exp[-(U_s(r_1) + U_s(r_2) + U_s(r_3))/kT] \\
&\quad \times (r_{12}^2r_{13}r_{23} + 3r_{12}r_{13}r_{23}) \} \, dr_1 \, dr_2 \, dr_3
\end{align*}
\] (4.20)

with the Mayer function:
\[
\begin{align*}
f_{ij} &= \exp[-U(r_{ij})/kT] - 1
\end{align*}
\] (4.21)
where the integrals are taken over the total volume of the container, \( V \).

Equation (4.17b) may be inverted by writing the new series with unknown coefficients \( A, B, C, D \ldots \) i.e. \( \frac{n_a}{P} = A + B n_a + C n_a^2 + D n_a^3 \); hence by making \( P \) the subject of this equation and back substituting into (4.17b) and finally equating the coefficients of the powers in \( n_a \), the following series is obtained:

\[
\frac{n_a}{P} = \frac{B_{AS}}{kT} + \frac{C_{AAS} n_a}{kTB_{AS}} + \frac{n_a^2}{B_{AS}^2} \left[ \frac{D_{AAS}}{kT} - \frac{C_{AAS}}{kTB_{AS}} \right] + \ldots
\]  

(4.22)

This may be used to determine the logarithmic form of the series adopted in the present work:

\[
\ln\left( \frac{n_a}{P} \right) = \ln\left( \frac{B_{AS}}{kT} \right) + \frac{C_{AAS} n_a}{B_{AS}^2} - \frac{3}{2} \frac{C_{AAS} n_a^2}{B_{AS}^4} + \frac{D_{AAS} n_a^2}{B_{AS}^6}
\]  

(4.23)

From (4.22):

\[
K_H = \frac{B_{AS}}{AkT}
\]  

(4.24)

hence:

\[
K_H = \frac{1}{AkT} \int_{V} \left[ \exp\left( -\frac{U_s(\hat{r})}{kT} \right) - 1 \right] d\hat{r}
\]  

(4.25)

The two-dimensional equation of state (Morrison and Ross 1973, Steele 1967) is the low temperature limit of (4.22).

\[
\frac{\phi A}{n a kT} = 1 + B_{2D} \left[ \frac{n_a}{A} \right] + C_{2D} \left[ \frac{n_a^2}{A} \right]^2 + \ldots
\]  

(4.26a)

where \( \phi \) is the two-dimensional spreading pressure and \( B_{2D}, C_{2D}, \ldots \) the two-dimensional virial coefficients. This series is obtained by making the two-dimensional approximation (see Steele 1967) and in this limit the two-dimensional virial coefficient may be written...
in terms of the gas-solid virial coefficients:

\[ \ln \left( \frac{n}{P} \right) = \ln \frac{N}{V} - 2B_{2D} \left( \frac{n}{A} \right) - \frac{3}{2} C_{2D} \left( \frac{n}{A} \right)^2 \ldots \]  

(4.26b)

then

\[ - \frac{C_{AAS}}{B_{AS}^2} \rightarrow \frac{2B_{2D}}{A} \]

where

\[ \frac{C_{AAS}}{B_{AS}^2} = \left\{ \int \left[ \exp \left[ -\left( U_s(r_1) + U_s(r_2) \right)/kT \right] f_{12} \, dr_1 \, dr_2 \right] \right\}^2 \]

(4.27)

Steele and Derderian (1972) have written the two-dimensional virial isotherm incorrectly (Steele, private communication). This should be expressed:

\[ \frac{n}{P} = \frac{B_{AS}}{kT} + n_a \left( \frac{-2B_{2D}}{A} \right) \frac{B_{AS}}{kT} + \frac{n_a^2}{2} \left( \frac{4B_{2D}^2}{A^2} - \frac{3C_{2D}}{A^2} \right) \frac{B_{AS}}{kT} \]

(4.26c)

The signs in (4.26b) are correct and differ to those given by Steele (1973b) but are in agreement with the result obtained by using (4.26c) to obtain (4.26b).

Equation (4.26b) is adopted in the present work, although the virial coefficients that are calculated are not always two-dimensional virial coefficients since in calculating the effect of the adsorbent potential field in the calculation of \( B_{2D} \) the integrals are over the adsorption volume, \( V_a \); also the effects of the two-dimensional approximation on the evaluation of (4.27) is investigated (see §4.8).

Equation (4.27) may be reduced if \( U_s(r_1) \gg kT \) at \( z^0 \).
\[
\left\{ \int_{V} \left[ \exp \left( \frac{U_s(r_1)}{kT} \right) - 1 \right] \, dr_1 \right\}^2 = \\
\int_{V_a} \int \exp \left[ \left( U_s(r_1) + U_s(r_2) \right) / kT \right] \, dr_1 \, dr_2
\]

The numerator of (4.27) may also be written as an integral over the adsorption volume, \( V_a \), (see Appendix 1).

\[
\frac{2B_{2D}}{A} = \frac{\int_{V_a} \int \exp \left[ \left( -U_s(r_1) + U_s(r_2) \right) / kT \right] \, f_{12} \, dr_1 \, dr_2}{\int_{V_a} \int \exp \left[ \left( U_s(r_1) + U_s(r_2) \right) / kT \right] \, dr_1 \, dr_2}
\]

\[
\frac{3C_{2D}}{A^2} = \int_{V_a} \int \int \exp \left[ \left( -U_s(r_1) + U_s(r_2) + U_s(r_3) \right) / kT \right] \, f_{12} \, f_{13} \, f_{23} \, dr_1 \, dr_2 \, dr_3
\]

\[
\times \left| \int_{V_a} \int \int \exp \left[ \left( -U_s(r_1) + U_s(r_2) + U_s(r_3) \right) / kT \right] \, dr_1 \, dr_2 \, dr_3 \right|^{-1}
\]

Equation (4.29) and (4.30) will be reduced later to enable the evaluation \( B_{2D} \) and \( C_{2D} \).

4.3 THE TWO-DIMENSIONAL FOURIER SERIES REPRESENTATION OF \( U_s(r) \)

4.3.1 Introduction

The integrals in (4.30) and (4.29) include the total potential energy field interaction, \( U_s(r) \). This consists of the electrostatic field contribution, \( U_e \), and the sum of the pairwise gas-ion interactions, \( U_d \). The expansion of \( U_e \) has already been given in §3.2.1.
and §3.2.2. The direct summation to determine $U_s^d$ of §3.5.2 is no longer possible because of the large amount of computing time necessary to perform the integrations. For the determination of $U^0$, the direct summation method is most efficient.

Steele (1973b) has extended Hill and Greenschlag's (1961) expansion of $U_s^d(r)$ such that for an atom at $(r,z)$, the value of $U_s^d(r)$ is given by:

$$U_s^d(r) = \sum_{\mathbf{g}} W(z) \exp(i\mathbf{g} \cdot \mathbf{r})$$  \hspace{1cm} (4.31)

where the vector $\mathbf{g} = 2\pi(\mathbf{g}_1 b_1 + \mathbf{g}_2 b_2)$

$$W(z) = \begin{cases} \frac{1}{\sqrt{2}} & z = \frac{1}{2}a_1 \text{ or } \frac{1}{2}a_2 \\ \frac{1}{\sqrt{2}} & z = \frac{1}{2}a_3 \\ 0 & \text{otherwise} \end{cases}$$ \hspace{1cm} (4.32)

with $b_1$ and $b_2$ the reciprocal lattice vectors, (Ziman 1972), defined below, and $g_1$, $g_2$ are integers. The surface plane vector may be written in the usual manner:

$$l = g_1 a_1 + g_2 a_2$$  \hspace{1cm} (4.33)

where $a_1$ and $a_2$ are the lattice periods in the surface plane. For a periodic lattice:

$$\exp[i\mathbf{g}(1 + L)] = \exp(i\mathbf{g}L)$$  \hspace{1cm} (4.34)

where $L = l_1 a_1 + l_2 a_2$ and $l_1$, $l_2$ are integers. From (4.34) $\exp(i\mathbf{g}L) = 1$. This means that the following relationships must hold:

$$b_1 \cdot a_1 = 1 \quad ; \quad b_2 \cdot a_2 = 1$$
$$b_1 \cdot a_2 = 0 \quad ; \quad b_2 \cdot a_1 = 0$$

These properties are satisfied by the reciprocal vectors:

$$b_1 = \frac{a_2 a_3}{a_1 a_2 a_3} \quad ; \quad b_2 = \frac{a_3 a_1}{a_1 a_2 a_3} \quad ; \quad b_3 = \frac{a_1 a_2}{a_1 a_2 a_3}$$

Hove and Krumhansl (1953) have derived a general expression for
\[ W(z) = \sum_{\beta} \sum_{k=1}^q \exp(i\beta k \beta) \sum_{\xi_1, \xi_2} \left[ U^d(r_{12}) \exp[-2\pi i(\xi_1^+ + \xi_2^+)] \right] d\xi_1 d\xi_2 \]  
\hspace{1cm} (4.35)

with \[ r_{12}^2 = a(\xi_1^2 + \xi_2^2 + z_\beta^2)^{\frac{1}{2}} \]

where \( a \) is the period of the cubic lattice.

\( z_\beta^* = z_\beta/a \) the reduced distance of the adsorbed atom from the \( \beta \) ion plane.

\( k \) labels the ions within the unit cell which are also in the \( \beta \) plane.

\( \xi_1 \) and \( \xi_2 \) are dummy variables.

The main difficulty in the evaluation of (4.35) is the integral:

\[ E(g, z_\beta^*) = \sum_{\xi_1, \xi_2} \left[ U^d[a(\xi_1^2 + \xi_2^2 + z_\beta^2)^{\frac{1}{2}}] \right] \times \]

\[ \exp[-2\pi i(\xi_1^+ + \xi_2^+)] d\xi_1 d\xi_2 \]  
\hspace{1cm} (4.36)

4.3.2 The Calculation of \( E(g, z_\beta^*) \) for \( U^\text{dis} \)

Equation (4.36) may be evaluated in two parts corresponding to the attractive and repulsive regions of \( U^d(r_{12}) \). In this case \( U^\text{dis} \) may be written in the general form:

\[ U^\text{dis} = \frac{\lambda}{x^{2n}} \]  
\hspace{1cm} (4.37)

where \( n = 3 \) and \( \lambda = C \) if (2.34) is used. However if \( n \) is maintained as an integer, the development will also be valid for the bi-reciprocal potential of §2.4.

For a semi-infinite lattice (4.36) gives
where $E_1$ is the contribution through (4.37) to $E$. The first transform may be obtained with the aid of the compilation of Campbell and Foster (1951). For $g \neq 0$

$$E_1(g, z_\beta^*) = \frac{\lambda}{a^{2n}} c_1 I$$  \hspace{1cm} (4.39)

where

$$c_1 = \left(\frac{4\pi^2}{n-1}\right)^{2n-\frac{1}{2}} (n-1)!! \left(\frac{1}{(4\pi)^{n-\frac{1}{2}}} \right)$$  \hspace{1cm} (4.40)

and

$$I = \int_{-\infty}^{+\infty} \frac{K_{n-1} \left\{2\pi g_1 (\xi_1^2 + z_\beta^*)^{\frac{1}{2}} \right\}}{(\xi_2^2 + z_\beta^*)^{\frac{1}{2}n-\frac{3}{2}}} \exp(-2\pi i g_2 \xi_2) d\xi_2$$  \hspace{1cm} (4.41)

where $K$ is a modified Bessel function in the standard notation. In a similar manner (4.41) may be evaluated. This reduces (4.39) to:

$$E_1(g, z_\beta^*) = \frac{\lambda}{a^{2n}} z_\beta^* (1-n) (g_1^2 + g_2^2)^{\frac{1}{2}n-\frac{1}{2}} \left(\frac{-1}{n-1}\right)^{2n} 2\pi^n$$

$$\times K_{1-n} \left[2\pi g_\beta^* (g_1^2 + g_2^2)^{\frac{1}{2}} \right]$$  \hspace{1cm} (4.42)

For $n = 3$ and $g^* = g.a = 2\pi (g_1^2 + g_2^2)^{\frac{1}{2}}$ where $g = |g|$, (4.42) gives:

$$E_1(g^* z_\beta^*) = \frac{\lambda a}{6} \left[\frac{g^*}{2z_\beta^*}\right] 2 K_2(g^*, z_\beta^*)$$  \hspace{1cm} (4.43)

for $g \neq 0$ where $K_2$ is the modified Bessel function of the second kind of order two.
For the case of $g = 0$, $E_1(g^*, z^*_B)$ may be obtained using standard integrals, (Spiegel 1968):

$$E_1(g^*, z^*_B) = \frac{\lambda \pi}{2a} \delta(z^*_B)$$ for $g_1 = g_2 = 0 \quad (4.44)$

4.3.3 The Calculation of $E(g, z^*_B)$ for $U^{\text{rep}}$

The LJ function that has previously been used by a number of researchers may be substituted into (4.42) to yield the inverse twelfth power transform with $n = 6$. Here the BM equation is adopted.

$$U^{\text{rep}} = c_1 \exp(-c_2 r) \quad (4.45)$$

The corresponding transform may be written:

$$E_2(g, z^*_B) = c_1 \int_{-\infty}^{\infty} \exp(2\pi i g_\xi_2) d\xi_2 \int_{-\infty}^{\infty} \exp(2\pi i g_\xi_1) \times \exp\left[-c_2 a (\xi_1^2 + \xi_2^2 + z^*_B)^{\frac{3}{2}}\right] d\xi_1 \quad (4.46)$$

The first integral may be evaluated, (Campbell and Foster 1951), and simplified to give the result:

$$E_2(g, z^*_B) = \frac{c_1 c_2 a}{\pi B} \int_{-\infty}^{\infty} (\xi_2^2 + z^*_B)^{\frac{3}{2}} \exp(2\pi i g_\xi_2) d\xi_2$$

where

$$B = \left[ g_1^2 + \frac{c_2 a^2}{4\pi^2} \right]$$

(4.47)

Similarly the final integral over $\xi_2$ yields the result for all $g$.

$$E_2(g, z^*_B) = \frac{c_1 c_2 a}{4\pi^2} \left[ \left( 1 + 2\pi z^*_B \right) \right] \exp(-2\pi z^*_B t) \quad (4.48)$$
where \( t = \left( \varepsilon_1^2 + \varepsilon_2^2 + a^2 \varepsilon_2^2 / 4 \pi^2 \right)^{\frac{1}{4}} \)  \hspace{1cm} (4.48)

The total transform for \( U^d(r) \) may be expressed:

\[
E(\varepsilon, z^*) = E_1(\varepsilon, z^*) + E_2(\varepsilon, z^*)
\]

\hspace{1cm} (4.49)

4.3.4 Application to the Sodium Chloride Type Structure

The problem of computing the \( W(z) \) coefficients from (4.35) may be reduced by a consideration of two interlacing face-centred cubic structures. If the cation is placed at the origin of the coordinate system, as shown in fig. 4.1, the positions of the other ions follows.

\[
W_{1\beta}(z^*) = W^C_{\beta}(z^*) + W^A_{\beta}(z^*)
\]

\hspace{1cm} (4.50)

where the superscripts label the cation and anion contributions to \( W_{1\beta}(z^*) \).

**Fig. 4.1**

![Diagram of Sodium Chloride Type Structure](image)

Key: • cation    ○ anion

The individual lattice layer contributions may be summed in (4.35) to yield \( W_{1\beta} \).
\[ W_g^C = \{1 + \cos[\pi(g_1 + g_2)]\} \sum_{\beta \text{ odd}} E_g^C(g, z_\beta^*) \]
\[ = \{\cos(\pi g_1) + \cos(\pi g_2)\} \sum_{\beta \text{ even}} E_g^C(g, z_\beta^*) \]  \hspace{1cm} (4.51)

\[ W_g^A = \{1 + \cos[\pi(g_1 + g_2)]\} \sum_{\beta \text{ even}} E_g^A(g, z_\beta^*) \]
\[ + \{\cos(\pi g_1) + \cos(\pi g_2)\} \sum_{\beta \text{ odd}} E_g^A(g, z_\beta^*) \]  \hspace{1cm} (4.52)

These are general expressions that can be used for both ideal and relaxed systems, and only involve the correct choice of $z_\beta^*$. The entire method could be developed for any lattice structure.

Once the coefficients $W_g(z^*)$ have been determined for a number of $g$ values, the quadratures over the $\mathbf{r}$ plane are much easier. The only limitations are whether the method can be put in a form suitable for efficient programming and this largely depends on the convergence of the sums over $\beta$ and indeed the convergence of the original Fourier series (4.31).

### 4.3.5 The Gas-Ion Interaction Parameters

Three interaction potential functions have been adopted. These have been discussed in §2.10. They all use the Toxvaerd and Praestgaard (1968) "exp6" equation for the argon self-interaction, together with the combining rules. The models are:

**MODEL A:** The parameters used in Chapter 3. The ion dispersion constants of Mayer (1933) with Tosi and Fumi's (1964) Born-Mayer parameters.

**MODEL B:** The Kirkwood-Müller dispersion constants for the ions combined with the derived repulsion constants (§2.10.2).
MODEL C: The Slater-Kirkwood dispersion constants, with the electron numbers of the ions taken from the corresponding inert gas electron core (Wilson 1965), combined with the derived Born-Mayer constants. (§2.10.2).

Unless otherwise stated, the calculations presented refer to the use of model A.

Table 4.1 presents the argon-ion parameters for the "exp6" equation.

<table>
<thead>
<tr>
<th>system</th>
<th>ε/k</th>
<th>r_m/nm</th>
<th>α</th>
<th>σ/nm</th>
<th>r_max/nm</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/Na⁺</td>
<td>10.450</td>
<td>0.4120</td>
<td>18.71</td>
<td>0.3743</td>
<td>0.0359</td>
<td>Tosi and Fumi (1964)</td>
</tr>
<tr>
<td>Ar/Na⁺</td>
<td>9.092</td>
<td>0.4217</td>
<td>18.71</td>
<td>0.3831</td>
<td>0.0368</td>
<td>Fumi and Tosi (1964)</td>
</tr>
<tr>
<td>Ar/Na⁺</td>
<td>8.739</td>
<td>0.4246</td>
<td>18.76</td>
<td>0.3858</td>
<td>0.0367</td>
<td>model B</td>
</tr>
<tr>
<td>Ar/Na⁺</td>
<td>1.366</td>
<td>0.5427</td>
<td>14.84</td>
<td>0.4849</td>
<td>0.0940</td>
<td>model C</td>
</tr>
<tr>
<td>Ar/Cl⁻</td>
<td>148.97</td>
<td>0.3735</td>
<td>16.96</td>
<td>0.3370</td>
<td>0.0441</td>
<td>Tosi and Fumi (1964)</td>
</tr>
<tr>
<td>Ar/Cl⁻</td>
<td>158.92</td>
<td>0.3706</td>
<td>16.44</td>
<td>0.3337</td>
<td>0.0479</td>
<td>Fumi and Tosi (1964)</td>
</tr>
<tr>
<td>Ar/Cl⁻</td>
<td>188.21</td>
<td>0.3665</td>
<td>16.19</td>
<td>0.3296</td>
<td>0.0496</td>
<td>model B</td>
</tr>
<tr>
<td>Ar/Cl⁻</td>
<td>274.84</td>
<td>0.3357</td>
<td>10.54</td>
<td>0.3325</td>
<td>0.1593</td>
<td>model C</td>
</tr>
</tbody>
</table>

4.3.6 Computation of the Fourier Coefficients

The expression for $E_1(g,z\beta)$ contains modified Bessel functions of the second kind. It is convenient to write the higher order functions in terms of the first and zero order Bessel functions. This may be done by using the recurrence relationship:
\[ K_{n+1}(x) = K_{n-1}(x) + \frac{2n}{x} K_n(x) \]  
\[ \text{Hence} \quad K_2(g^*z_\beta^*) = K_0(g^*z_\beta^*) + \frac{2}{g^*z_\beta^*} K_1(g^*z_\beta^*) \]  
\[ K_2(g^*z_\beta^*) = K_0(g^*z_\beta^*) \left[ 1 + \frac{72}{(g^*z_\beta^*)^2} + \frac{324}{(g^*z_\beta^*)^4} \right] \]  
\[ + K_0(g^*z_\beta^*) \left[ \frac{12}{(g^*z_\beta^*)^3} + \frac{192}{(g^*z_\beta^*)^3} \right] \]  

It is also apparent on examining the \( W_g \) and \( E(g,z_\beta^*) \) expressions that many terms in the series (4.31) are equivalent. Table 4.2 shows the \( g_1, g_2 \) values and the number of terms that are equal (shown by the degeneracy factor, \( \gamma_n \)).

**TABLE 4.2 DEGENERACY FACTORS, \( \gamma_n \), FOR THE DIFFERENT \( g_1 \) AND \( g_2 \) VALUES**

<table>
<thead>
<tr>
<th>( g_1 )</th>
<th>( g_2 )</th>
<th>( n )</th>
<th>( \gamma_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

It is essential to incorporate this knowledge into the programming.
so that repetitive calculations are not performed.

The convergence of the individual series was tested. For (4.51) and (4.52) with \( g \neq 0 \), only 1 term was used. With \( g = 0 \), 20 terms were required. In the case of the original Fourier series, convergence to 4 digits was obtained by using 113 terms in (4.31) corresponding to:

\[
(g_1, g_2) : \quad g_1 = 0 \quad g_2 = 0 \Rightarrow 5 \\
g_1 = 1 \quad g_2 = 0 \Rightarrow -4 \\
g_1 = 2 \quad g_2 = 0 \Rightarrow -3 \\
g_1 = 3 \quad g_2 = 0 \Rightarrow -2 \\
g_1 = 4 \quad g_2 = 0, 1 \\
g_1 = 5 \quad g_2 = 0
\]

The values of \( u_s(r) \) were checked against a direct summation and found to be in agreement. The potential energy contour map at a position \( z \) above the surface also exhibited the correct symmetry. This was taken to validate the entire mathematical derivations outlined so far in this chapter.

4.4 THE SECOND TWO-DIMENSIONAL VIRIAL COEFFICIENT

The expression for \( B_{2D} \), (4.29), involves \( \exp[-(U_s(r)/kT)] \).

Since \( U_s(r) \) is a periodic potential field, it may be expressed in terms of a Fourier series. This property also extends to any function of \( U_s(r) \).

\[
\exp[-U_s(r)/kT] = \sum_{\mathbf{g}} e_g(z) \exp(i\mathbf{g} \cdot \mathbf{r}) \quad (4.56)
\]

Equation (4.56) is analogous to (4.31) except that \( e_g(z) \) are now the Fourier coefficients and are dependent on temperature. In this case to be consistent with earlier sections the vector \( g \) must have
the same meaning as in (4.32). The coefficients are thus:

\[ e_{\xi}(z) = \frac{1}{A} \int \exp[-U_s(x)/kT] \exp[i\xi T] d\xi \]  

(4.57)

where \( A \) is the surface area. This simplifies to:

\[ e_{\xi}(z) = \frac{1}{\sigma_A} \int \exp[-U_s(x)/kT] \exp(i\xi \cdot \mathbf{r}) d\mathbf{r} \]  

(4.58)

\[ \leftrightarrow = \left\{ \exp[-U_s(x)/kT] \cos(\xi \cdot \mathbf{r}) d\mathbf{r}_1 d\mathbf{r}_2 \right\} \]  

(4.59)

where \( \sigma_A \) is the area of the unit cell (= \( a^2 \)).

If \( e_{\xi}(z) \) is substituted into (4.29), then

\[- \frac{2B_{2D}}{A} = \left\{ \sum_{\xi \in \xi} \int_{V_a} \int \sum_{\xi' \in \xi'} e_{\xi}(z_1) e_{\xi'}(z_2) \exp[i(\xi \cdot \mathbf{r}_1 + \xi' \cdot \mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 dz_1 dz_2 \right\}^{-1} \]

(4.60)

Following Steele (1973b), (4.60) may be reduced as follows. The integrations over \( r_1 \) and \( r_2 \) in the denominator are zero for \( \xi \) and \( \xi' \neq 0 \) because of the \( \exp[i(\xi \cdot \mathbf{r}_1 + \xi' \cdot \mathbf{r}_2)] \) term. The integral in the numerator can be evaluated by a change in variables:

\[ \xi \cdot \mathbf{r} = \frac{1}{2}(\xi + \xi') \mathbf{r}_{cm} + \frac{1}{2}(\xi - \xi') \mathbf{r}_{12} \]  

(4.61)

where

\[ \mathbf{r}_{cm} = \mathbf{r}_1 + \mathbf{r}_2 \]

\[ \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 \]  

(4.62)

The integrals over \( r_1 \) and \( r_2 \) may be replaced by those over \( r_{12} \) and
Since \( f_{12} \), (4.21), is independent of \( \tau_{cm} \), the integral over \( \tau_{cm} \) may be evaluated.

\[
B_{2D} = -\frac{1}{2} \left\{ \iiint e_{G}^{i} e_{G}^{j} f_{12} \exp(ig \cdot \tau_{12}) d\tau_{12} dz_{1} dz_{2} \right\} \\
	imes \left[ \iint e_{0}^{i} e_{0}^{j} dz_{1} dz_{2} \right]^{-1} \tag{4.63}
\]

The integrals are over the thickness of the adsorbed layer.

The inert gas self-interaction dependent part of (4.63) may be separated as the two-dimensional Fourier transform of the Mayer function, \( f_{12} \):

\[
f(g, z_{12}) = \frac{1}{2\pi} \int_{A} f_{12} \exp(ig \cdot \tau_{12}) d\tau_{12} \tag{4.64}
\]

Steele (1973b) presents (4.64) and then quotes (4.68). This step may be accomplished by transforming to polar coordinates:

\[
d\tau_{12} = \tau_{12} d\tau_{12} d\theta \tag{4.65a}
\]

where \( \tau_{12} \) is the radial ordinate and \( \theta \) the azimuth. If the corresponding azimuth for the \( g \) vector is \( \phi \) (4.64) becomes:

\[
f(g, z_{12}) = \frac{1}{2\pi} \int_{0}^{\infty} f_{12} \tau_{12}^{2} d\tau_{12} \int_{0}^{2\pi} \cos[g \tau_{12} \cos(\theta - \phi)] d\theta \tag{4.65b}
\]

where \( g = |g| \) and \( \tau_{12} = |\tau_{12}| \). By writing \( \cos(\theta - \phi) = \sin(\pi/2 + \theta - \phi) = \sin \omega \), (4.65b) may then be expressed in the convenient form:

\[
f(g, z_{12}) = \frac{1}{2\pi} \int_{0}^{\infty} f_{12} \tau_{12}^{2} d\tau_{12} \int_{0}^{2\pi} \exp[i g \tau_{12} \sin \omega] d\omega \tag{4.66}
\]

This is permissible since \( \phi \) is a constant and the integral is over
1 cycle. The only assumption implicit in (4.66) is that $f_{12}$ is independent of the relative orientation of the two atoms. The general result:

$$
2\pi \int_0^{2\pi} \cos(g \tau_{12} \sin \theta) d\theta = 2\pi J_0(g \tau_{12})
$$

(4.67)

yields

$$
f(g,z_{12}) = \int_0^{\tau_{12}} J_0(g \tau_{12}) d\tau_{12}
$$

(4.68)

Thus (4.63) becomes:

$$
B_{2D} = \frac{-\pi \sum \int \int e_0(z_1)e_0(z_2)f(g,z_{12})dz_1dz_2}{\int \int e_0(z_1)e_0(z_2)dz_1dz_2}
$$

(4.69)

where the $z$ integrals are taken over the adsorption volume.

Since the atoms in the adsorbed layer are likely to be confined to an almost planar region located at the potential energy minimum, i.e. $z_{12}$ is small, the Bessel transform, (4.68), may be expanded in a Taylor's series.

$$
f(g,z_{12}) = f(g,0) + (z_1 - z_2)f'(g,0) + \frac{1}{2}(z_1 - z_2)^2f''(g,0) + \ldots
$$

(4.70)

This is commonly called the two-dimensional approximation. The leading term in (4.70) is taken as the first approximation to $f(g,z_{12})$. The second term, $[(z_1 - z_2)f'(g,0)]$, is zero and only the terms containing $f''(g,0)$ and $f'''(g,0)$ are non-zero. Their contribution to $B_{2D}$ will be examined in §4.8, meanwhile the first term in (4.70) when substituted into (4.69) yields:

$$
B_{2D} = -\pi \sum \frac{f(g,0)e_{z_1}^2/e_{0}^2}{G}
$$

(4.71)

where

$$
e_{G} = \int e_G dz
$$

(4.72)
with the integral over the adsorption volume.

4.5 APPLICATION OF THE VIRIAL EXPANSION TO A STRUCTURELESS SURFACE

A surface with a potential field independent of \( \frac{\pi}{\Delta} \), i.e. \( \langle e \rangle = 0 \) for all \( \vec{g} \neq 0 \), is in the present work called a structureless surface. In this case:

\[
B_{2D} = -\pi f(\vec{g}, 0)
\]  

(4.73)

and the reduced two-dimensional second virial coefficient may be expressed:

\[
B_{2D}^0 = B_{2D}/\pi r_m^2
\]  

(4.74)

\[ \leftrightarrow \quad B_{2D}^0 = -f(0^+) \]  

(4.75a)

where

\[
f(\vec{g}^+) = \int_0^\infty J_0(\vec{g}^+ \tau^+) f(\tau^+) \tau^+ d\tau^+
\]  

(4.75b)

\[
\leftrightarrow \quad f(\vec{g}) = \frac{1}{r_m^2} f(\vec{g})
\]  

(4.76)

where \( \vec{g} = |\vec{g}| \), \( \vec{g}^+ = \vec{g}r_m \) and \( \tau^+ = \tau/r_m \).

Using the method described by Steele (1973b), the reduced two-dimensional third virial coefficient for a structureless surface, may also be written:

\[
c_{2D}^0 = -\frac{4}{3} \int_0^\infty \left[ f(\vec{g}^+) \right]^3 \vec{g}^+ d\vec{g}^+
\]  

(4.77a)

\[
\leftrightarrow \quad c_{2D}^0 = \frac{c_{2D}}{\pi^2 r_m^4}
\]  

(4.77b)

The calculation of \( B_{2D}^0 \) and \( c_{2D}^0 \) was programmed in Algol 60 and subsequently tested by comparing the results with those of Steele (1973b) and Morrison and Ross (1973). An example of the function that was integrated for the computation of \( f(\vec{g}^+) \) is presented in fig. 4.2.
Fig. 4.2 Function contributing to the Bessel transform of the Mayer function i.e.,

\[ f(g^+) = \int_0^{\infty} J_0(h^+ \tau) f(\tau) \tau^+ \, d\tau^+ \]

where \( g^+ = g r_m \) and \( \tau^+ = \tau / r_m \).
Fig. 4.3 The dependence of the Bessel transform of the Mayer function on $g^+; T^+ = kT/\epsilon$. 

\[ f(g^+)/s^2 \]
The integral is rapidly convergent because \( \lim_{\tau \to \infty} f(g^\tau) = 0 \) and \( J_0(g^\tau, \tau^\dagger) \) is rapidly oscillating. The \( f(g^\tau) \) function that contributes to \( (4.77) \) also oscillates and diminishes to zero at large \( g^\tau \) values (see fig. 4.3). The integrals were determined by the quadrature formulae of Patterson (1968) for the rapidly fluctuating functions, or of Clenshaw and Curtis (1965) for the simpler curves. These are convenient methods that minimize the machine time for the computations, and at the same time allow specified accuracy limitations to be imposed upon the calculation. The majority of the integrals were determined by dividing the entire integral range into sections. Each of these sections was integrated separately to a specified relative accuracy of \( 10^{-6} \). Both the width of each section and the upper integral limit was determined by the behaviour of the function and the rate of the integral convergence. Error "flags" were used to notify the programmer of any failure to reach the accuracy requirements during any section of the integration.

Since both Steele (1973b) and Morrison and Ross (1973) used the LJ interaction potential function, this was used in the testing procedure. The resulting \( B_{2D}^0 \) values are shown as a function of \( T^\dagger \) in Table 4.3 and are found to be in agreement with the results of Steele (1973b) and Morrison and Ross (1973). The computation of \( C_{2D}^0 \) required considerably more machine time, (6 minutes on an ICL 1904A for one value), and so was limited to four determinations. These were at \( T^\dagger = 1.0, 2.0, 3.0, 4.0 \) and showed exact agreement with the values of Steele (1973b) but for \( T^\dagger \leq 2.0 \) differences of the order of 0.9% were found on a comparison with the evaluations of Morrison and Ross (1973). Since no reason could be found for this discrepancy, the results of Morrison and Ross (1973) are thought to be in slight error.
<table>
<thead>
<tr>
<th>$T^+$</th>
<th>$B_{2D}^0$</th>
<th>$T^+$</th>
<th>$B_{2D}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>-7.0631</td>
<td>2.3</td>
<td>+0.1591</td>
</tr>
<tr>
<td>0.4</td>
<td>-3.2439</td>
<td>2.4</td>
<td>+0.1718</td>
</tr>
<tr>
<td>0.5</td>
<td>-1.9054</td>
<td>2.5</td>
<td>+0.1833</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.2555</td>
<td>2.6</td>
<td>+0.1938</td>
</tr>
<tr>
<td>0.7</td>
<td>-0.8788</td>
<td>2.7</td>
<td>+0.2033</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.6353</td>
<td>2.8</td>
<td>+0.2120</td>
</tr>
<tr>
<td>0.9</td>
<td>-0.4699</td>
<td>2.9</td>
<td>+0.2200</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.3416</td>
<td>3.0</td>
<td>+0.2273</td>
</tr>
<tr>
<td>1.1</td>
<td>-0.2468</td>
<td>3.1</td>
<td>+0.2341</td>
</tr>
<tr>
<td>1.2</td>
<td>-0.1723</td>
<td>3.2</td>
<td>+0.2404</td>
</tr>
<tr>
<td>1.3</td>
<td>-0.1122</td>
<td>3.3</td>
<td>+0.2462</td>
</tr>
<tr>
<td>1.4</td>
<td>-0.0628</td>
<td>3.4</td>
<td>+0.2517</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.0216</td>
<td>3.5</td>
<td>+0.2567</td>
</tr>
<tr>
<td>1.6</td>
<td>+0.0132</td>
<td>3.6</td>
<td>+0.2614</td>
</tr>
<tr>
<td>1.7</td>
<td>+0.0432</td>
<td>3.7</td>
<td>+0.2658</td>
</tr>
<tr>
<td>1.8</td>
<td>+0.06915</td>
<td>3.8</td>
<td>+0.2699</td>
</tr>
<tr>
<td>1.9</td>
<td>+0.09177</td>
<td>3.9</td>
<td>+0.2738</td>
</tr>
<tr>
<td>2.0</td>
<td>+0.11167</td>
<td>4.0</td>
<td>+0.2774</td>
</tr>
<tr>
<td>2.1</td>
<td>+0.1293</td>
<td>4.1</td>
<td>+0.2808</td>
</tr>
<tr>
<td>2.2</td>
<td>+0.1450</td>
<td>4.2</td>
<td>+0.2840</td>
</tr>
</tbody>
</table>
Mason and Rice (1954) have listed parameters for the LJ and the "exp6" functions. Since these parameters are derived from similar sources of experimental data, it is fair to compare the derived two-dimensional virial coefficients at 77.5K. This is done in Table 4.4 for the inert gases and shows that the differences can be as high as 5.3% but they can be smaller. The value of $B_{2D}$ for argon shown in Table 4.4, compares poorly with the value derived from the TP "exp6" equation for argon. At 77.5K this gives a $B_{2D}$ value of $-54.2 \, \text{R}^2 \, \text{atom}^{-1}$ which illustrates the importance of the choice of the parameters for any interaction potential function that is adopted.

**TABLE 4.4 A COMPARISON OF THE $B_{2D}$ VALUES OBTAINED FOR SOME INERT GASES AT 77.5K BY USING THE "EXP6" AND LJ INTERATOMIC POTENTIAL ENERGY FUNCTIONS**

<table>
<thead>
<tr>
<th>gas</th>
<th>&quot;exp6&quot;</th>
<th>LJ</th>
<th>% difference in $B_{2D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T^+$</td>
<td>$\alpha$</td>
<td>$r_{\text{max}} / R$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$/ \text{R}^2 , \text{atom}^{-1}$</td>
</tr>
<tr>
<td>Ne</td>
<td>2.039</td>
<td>14.5</td>
<td>0.1848</td>
</tr>
<tr>
<td>Ar</td>
<td>0.6291</td>
<td>14.0</td>
<td>0.2032</td>
</tr>
<tr>
<td>Kr</td>
<td>0.4896</td>
<td>12.3</td>
<td>0.2644</td>
</tr>
<tr>
<td>Xe</td>
<td>0.3352</td>
<td>13.0</td>
<td>0.2470</td>
</tr>
</tbody>
</table>

The discussion in Chapter 2 indicated that the "exp6" with the TP parameters is a reliable function for the argon self-interaction potential. This will be used in the remainder of this chapter; the results for the calculation of $B_{2D}^0$ and $C_{2D}^0$ are shown in Table 4.5.
TABLE 4.5 THE REDUCED TWO-DIMENSIONAL SECOND AND THIRD VIRIAL COEFFICIENTS FOR ARGON ON A STRUCTURELESS SURFACE

The "exp6" equation with parameters from Toxvaerd and Praëstgaard (1968), \((\alpha = 21.0 \quad T^* = kT/\varepsilon)\), was used.

<table>
<thead>
<tr>
<th>(T^*)</th>
<th>(B_{2D}^0)</th>
<th>(C_{2D}^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4610 ((T = 77.5 K))</td>
<td>-1.3731</td>
<td>+0.1656</td>
</tr>
<tr>
<td>0.3</td>
<td>-4.3760</td>
<td>-24.980</td>
</tr>
<tr>
<td>0.32</td>
<td>-3.6157</td>
<td>-12.604</td>
</tr>
<tr>
<td>0.34</td>
<td>-3.0437</td>
<td>-6.553</td>
</tr>
<tr>
<td>0.36</td>
<td>-2.6014</td>
<td>-3.432</td>
</tr>
<tr>
<td>0.38</td>
<td>-2.2514</td>
<td>-1.749</td>
</tr>
<tr>
<td>0.40</td>
<td>-1.9689</td>
<td>-0.8283</td>
</tr>
<tr>
<td>0.50</td>
<td>-1.1212</td>
<td>+0.2987</td>
</tr>
<tr>
<td>0.60</td>
<td>-0.7081</td>
<td>+0.2955</td>
</tr>
<tr>
<td>0.70</td>
<td>-0.4680</td>
<td>+0.2264</td>
</tr>
<tr>
<td>0.80</td>
<td>-0.3125</td>
<td>+0.1751</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.1244</td>
<td>+0.1207</td>
</tr>
<tr>
<td>1.2</td>
<td>-0.0157</td>
<td>+0.0984</td>
</tr>
<tr>
<td>1.4</td>
<td>+0.0547</td>
<td>+0.0885</td>
</tr>
<tr>
<td>1.8</td>
<td>+0.1397</td>
<td>+0.0830</td>
</tr>
<tr>
<td>2.0</td>
<td>+0.1671</td>
<td>+0.0827</td>
</tr>
</tbody>
</table>

The values of \(B_{2D}\) for argon obtained using the LJ function with parameters from Mason and Rice (1954) and the "exp6" with the TP parameters, are compared in fig. 4.4. Despite the fact that the Mason and Rice (1954) parameters for the LJ equation are very close to the widely adopted parameters presented in Hirschfelder, Curtiss and Bird (1954), the difference in the \(B_{2D}\) curves shown in fig. 4.4
Fig. 4.4 The temperature dependence of the two-dimensional second virial coefficient.

Key:
- • structureless (LJ) surface using the LJ potential function
- • structureless (exp6) surface using the "exp6" potential function
- ○ relaxed (100) NaCl structured surface
- - ideal (100) NaCl structured surface
will be of importance in any experimental analysis.

The results of the application of the "exp6" equation in fig. 4.4 also indicate a two-dimensional Boyle temperature, $T_B^{2D}$, higher than that obtained by applying the LJ equation. In the former case $T_B^{2D}$, calculated by Everett central difference interpolation from $E_0^{2D}$ versus $T$ values, is found to be 208.1 ± 0.05K. This result is in agreement with the value derived from the experimental bulk phase Boyle temperature (Munn 1964), $T_B^{3D}$, if the Hill-de Boer (see §5.2.1) and van der Waals models for the two-dimensional gas and bulk gas are adopted in the comparison ($T_B^{3D}/2 = T_B^{2D} = 205K$). The value that is obtained using the LJ formula is considerably lower (see fig. 4.4; $T_B^{2D} = 181K$).

4.6 THE GAS-SOLID PERTURBATION TERMS

If $U_s(r)$ is not independent of $r$, i.e. the surface is structured, the two-dimensional second virial coefficient may be expressed in a series (c.f. 4.71):

$$B_2^{2D} = -\pi f(0) - \pi \gamma \sum_{n=1}^{\infty} f(n) \frac{\langle e_n \rangle^2}{\langle e_0 \rangle^2}$$  \hspace{1cm} (4.78)

where the degeneracy factor, $\gamma_n$, is determined by:

- $g_1 = g_2 \quad \leftrightarrow \quad \gamma_n = 4$
- $g_1 \neq g_2 = 0 \quad \leftrightarrow \quad \gamma_n = 4$
- $g_1 \neq g_2 \neq 0 \quad \leftrightarrow \quad \gamma_n = 8$

where $n$ in the ascending sequence labels the ordered pairs $(g_1, g_2)$: $(1,0); (1,1); (2,0); (2,1); \ldots$ This corresponds to the degeneracy found in equation (4.31) for $W_g$.

The, $\pi \gamma_n f(n) \langle e_n \rangle^2 / \langle e_0 \rangle^2$, terms are called the gas-solid perturbation values and are additional terms to $-\pi f(0)$, discussed for a
structureless surface. These arise from the discrete periodic structure of the ionic surface.

The gas-solid perturbation values may be obtained from the integrals of $e_n(z)$ over $z$. The values of $e_n(z)$ can be determined from \(4.59\) by using \(4.31\) to calculate the $W_s$ value corresponding to the normal distance above the surface plane, $z$; hence the integral in \(4.59\) may be evaluated with a minimum of calculation. The $e_0$, $e_1$ and $e_2$ functions for argon adsorbed on the ideal (100) face of sodium chloride are shown on a logarithmic plot in fig. 4.5 for $T^t = 0.4610$ and $T^t = 1.0$. The functions are short ranged with the lower integral limit fixed by the convergence of the function to zero. This is expected from an examination of \(4.59\) when $U_s(r)$ becomes large and positive at small $z$. The upper integral limit is defined by the extent of the adsorption volume. In most cases the functions converge to zero for $z^*$, ($= z/a$), $< 1.0$. However in the case of $e_0(z^*)$, equation \(4.59\) indicates that $\lim_{z^* \to \infty} e_0(z^*) = 1$. In this case the adsorption volume is considered as that region where the gas density is substantially greater than the corresponding bulk phase gas value.

This condition may be expressed in the present context as that distance from the surface when $U_s(r) \to 0$ to within computing accuracy. In fact the magnitude of the $<e_o>$ value for $T < 120K$ is relatively insensitive to the precise upper integral limit. In general the lower and upper integral limits were taken as $z^* = 0.46$ and 1.0 respectively. At higher temperatures the adsorption volume approximation, discussed in Appendix 1, breaks down and the results become dependent on the choice of the upper integral limit. In this work, for $T > 120K$, the upper integral limit was set to $z^* = 5.0$ when $\exp[-U_s(r)] - 1 < 10^{-3}$. However the resulting values are not reliable and probably represent an over-estimation of the gas-solid perturbation terms.
Fig. 4.5 Variation of $e_n(z^*)$ with $z^*$ for the ideal (100) NaCl surface

Key:

- $T^* = 0.4610; T = 77.5K$
- using $\varepsilon$ from TP
- $T^* = 1.0$
- negative values of $e_n$
The integrals were determined by the methods discussed in §4.5. The program to evaluate $\langle e_n \rangle$ was written in Fortran IVD and because of the time requirements, was run on a CDC 7600 computer at Manchester University. The individual gas-surface perturbation terms for argon on ideal (100) sodium chloride at 77.5K are shown in Table 4.6.

**TABLE 4.6 THE RELATIVE CONTRIBUTION OF THE GAS-SOLID PERTURBATION TERMS TO THE TWO-DIMENSIONAL SECOND VIRIAL COEFFICIENT**

Argon adsorbed on ideal (100) sodium chloride at a temperature of: $T^\dagger = 0.4610$ (77.5K)

<table>
<thead>
<tr>
<th>n</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$-\pi \gamma f(n) \langle e_n^2 / \langle e \rangle^2 \rangle / 10^{-20} m^2$ atom$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-54.149</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>+0.3542</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>-7.7743</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0</td>
<td>-0.2747</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>1</td>
<td>+1.0255</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>+0.0016</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>0</td>
<td>-0.02513</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>1</td>
<td>-0.3558</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>2</td>
<td>-0.02934</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>3</td>
<td>+0.00952</td>
</tr>
</tbody>
</table>

The relative contribution of the first terms in (4.78) indicates that the $n = 1$ and $n = 2$ terms are the most important (giving an approximately 14% change in $B_{2D}$). As $T^\dagger$ increases, the $n = 1, 2$ values become more important; at $T^\dagger = 0.6$ the $n = 2$ term is 18% of the $n = 0$ term and the remaining contribution, i.e. $n > 2$, make a smaller relative change in $B_{2D}$. For example at $T^\dagger = 0.4610$, the $n = 3, 4$ and...
5 values are a total of 10.1% of the sum of the n = 1 and 2 terms compared to 4.3% at $T = 0.6$. Since in all cases the first two gas-solid perturbation terms are significant, they must be considered in the $B_{2D}$ calculation.

The gas-solid perturbation contributions to the two-dimensional second virial coefficient may also be calculated for argon on the relaxed (100) surface (see §3.6.1). The results of the $c_n$ calculations are shown in fig. 4.6. The difference in the potential field for the relaxed and unrelaxed systems, as discussed in Chapter 3, are quite dramatic for argon on sodium chloride, and are clearly evident in the comparison of the $n = 1$ and $n = 2$ terms for the two systems. The $n = 1$ term dominates the correction for the relaxed surface whereas the $n = 2$ term, (Table 4.6), is the major contribution in the unrelaxed case. This may be explained in physical terms of the surface field acting as a weighting factor to the Mayer function in the integrals for $B_{2D}$ and, as shown above, the field topology is very important in determining both the sign of the gas-solid perturbation to $B_{2D}$ and its magnitude. The localization that occurs as a result of the well depth in the $U_s(x)$ field gives an alteration in the average lateral interaction as compared to the unstructured surface.

The results for the ideal and relaxed (100) surface are illustrated in fig. 4.4. The values of $B_{2D}$ which were calculated using the first five perturbation terms at 77.5K are $-61.2 \times 10^{-20}$ m$^2$ atom$^{-1}$ for the ideal surface and $-42.9 \times 10^{-20}$ m$^2$ atom$^{-1}$ for the relaxed surface. These compare with $-54.2 \times 10^{-20}$ m$^2$ atom$^{-1}$ for the structureless surface.
Fig. 4.6 Variation of $e_n(z^*)$ with $z^*$ for the relaxed (100) NaCl surface. $T^+ = 0.4610$

Key: ● negative values of $e_n$
4.7 THE THIRD-BODY EFFECT

4.7.1 Introduction

The presence of the ionic surface may have some effect on the calculation of the Mayer function which will be reflected in the values of \( f(n) \) used in (4.78). The effect is primarily caused by the perturbation of the inert gas atoms electronic structure by the presence of the solid surface. It is analogous to the non-additivity term in the calculation of the bulk-gas third virial coefficient. In this work it is called the third-body effect and is mainly composed of two separate components; one arising from the induced dipole self-interaction of the argon atoms, and the second, a less well-defined non-electrostatic perturbation of the bulk phase argon self-interaction caused by mutually induced interactions between the gas atom and the solid. This latter perturbation may affect both the dispersion and repulsion components of the self-interaction potential.

4.7.2 The Third-Body Effect on the Non-Electrostatic Argon Self-Interaction

A number of theoretical treatments have been presented on this problem and they all indicate an increased repulsive interaction between gas atoms in the same \( z \) plane. Sinanoglu and Pitzer (1960) examined the third-body dispersion effect and concluded that the minimum of the potential energy function, \( \epsilon \), is decreased by 20-40% with \( r_m \) remaining unchanged. The above treatment used third-order perturbation theory with the perturbation Hamiltonian described by the usual type of multipole expansion discussed in §2.2.1 which is only valid when there are no overlap effects. Freeman (1975b), however, has used the Gordon-Kim density functional method, which is only valid when there is significant overlap between the atoms. The argon-graphitized carbon black system, (Freeman 1975b), showed a 13%
decrease in $\epsilon$ with no change in $r_m$. This result is close to that obtained by Everett (1965) who used a virial analysis on the experimental data from the same system. This is in contrast to the work of Morrison and Ross (1973) who made their virial analysis of the high temperature adsorption isotherms of argon on graphitized carbon blacks and found that the unperturbed bulk-gas parameters, used in the calculation of $B_{2D}$ and $C_{2D}$, gave an adequate description of the isotherms.

In view of these results and following Sams, Constabaris and Halsey (1962), the third-body effect is assumed to change the depth of the potential minimum, $\epsilon$, but not to change the position of the minimum, $r_m$. No prior knowledge of the change in $\epsilon$ is assumed, in fact the present analysis is carried out by assuming that this perturbation effect is negligible. If more data concerning the temperature dependence of $B_{2D}$ becomes available, it will be possible to include changes in $f(n)$ to account for the effects of the perturbation. For this reason, Table 4.7 is included to give the $f(n)$ values for a ±10% change in $T^+$ at 77.5K.

4.7.3 The Induced Dipole Self-Interaction

The classical dipole-dipole interaction of the gas atoms which result from the surface electric field polarization of the atoms, is given by:

$$U^{dd} = \mu_1 \mu_2 (\sin \theta_1 \sin \theta_2 \cos \phi_{12} - 2 \cos \theta_1 \cos \theta_2) / r_{12}^3$$

(4.79)

where $\mu_1$ and $\mu_2$ are the induced dipoles of the two atoms labelled '1' and '2', and $r_{12}$ is the distance between the two dipoles. The angles $\theta_1$ and $\theta_2$ are the angles of inclination of the dipole axis to the line of centres as reflected in the perpendicular plane, and $\phi_{12} = \phi_1 - \phi_2$ where $\phi_1$ and $\phi_2$ are the angles subtended between the
TABLE 4.7 CHANGES IN $f(h)$ FOR $\pm 10\%$ CHANGES IN $T^+$ AT 77.5K

Values for argon using TP "exp6" parameters

<table>
<thead>
<tr>
<th>$n$</th>
<th>$T^+$ (T=77.5K)</th>
<th>0.4610</th>
<th>0.4150</th>
<th>0.4250</th>
<th>0.4350</th>
<th>0.4450</th>
<th>0.4550</th>
<th>0.4650</th>
<th>0.4750</th>
<th>0.4850</th>
<th>0.4950</th>
<th>0.5050</th>
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<tr>
<td>3</td>
<td>0.942</td>
<td>1.322</td>
<td>1.223</td>
<td>1.134</td>
<td>1.054</td>
<td>0.982</td>
<td>0.917</td>
<td>0.858</td>
<td>0.804</td>
<td>0.755</td>
<td>0.710</td>
<td></td>
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<tr>
<td>5</td>
<td>-0.2884</td>
<td>-0.428</td>
<td>-0.391</td>
<td>-0.358</td>
<td>-0.329</td>
<td>-0.303</td>
<td>-0.280</td>
<td>-0.259</td>
<td>-0.240</td>
<td>-0.224</td>
<td>-0.209</td>
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</tr>
<tr>
<td>6</td>
<td>1.388</td>
<td>1.723</td>
<td>1.638</td>
<td>1.561</td>
<td>1.490</td>
<td>1.425</td>
<td>1.365</td>
<td>1.310</td>
<td>1.259</td>
<td>1.211</td>
<td>1.167</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.249</td>
<td>2.852</td>
<td>2.698</td>
<td>2.558</td>
<td>2.431</td>
<td>2.315</td>
<td>2.208</td>
<td>2.111</td>
<td>2.021</td>
<td>1.938</td>
<td>1.862</td>
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<td>8</td>
<td>0.410</td>
<td>0.544</td>
<td>0.509</td>
<td>0.478</td>
<td>0.449</td>
<td>0.424</td>
<td>0.402</td>
<td>0.381</td>
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<td>0.346</td>
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<td>-1.316</td>
<td>-1.249</td>
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<td>-1.133</td>
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<td>-1.036</td>
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<td>10</td>
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<td>-1.932</td>
<td>-1.830</td>
<td>-1.737</td>
<td>-1.653</td>
<td>-1.576</td>
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<td>-1.439</td>
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</tr>
<tr>
<td>11</td>
<td>-1.611</td>
<td>-2.076</td>
<td>-1.956</td>
<td>-1.848</td>
<td>-1.750</td>
<td>-1.661</td>
<td>-1.580</td>
<td>-1.506</td>
<td>-1.438</td>
<td>-1.375</td>
<td>-1.318</td>
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</tr>
<tr>
<td>12</td>
<td>0.028</td>
<td>0.044</td>
<td>0.041</td>
<td>0.037</td>
<td>0.033</td>
<td>0.030</td>
<td>0.026</td>
<td>0.023</td>
<td>0.020</td>
<td>0.017</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.068</td>
<td>1.380</td>
<td>1.300</td>
<td>1.227</td>
<td>1.161</td>
<td>1.102</td>
<td>1.047</td>
<td>0.998</td>
<td>0.953</td>
<td>0.911</td>
<td>0.873</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-0.955</td>
<td>-1.253</td>
<td>-1.176</td>
<td>-1.107</td>
<td>-1.044</td>
<td>-0.987</td>
<td>-0.936</td>
<td>-0.889</td>
<td>-0.845</td>
<td>-0.806</td>
<td>-0.769</td>
<td></td>
</tr>
</tbody>
</table>
polar axes and the perpendicular passing through their centres.

Since the derivation of $f(g, 0)$ has already assumed the independence of $r_{12}$ on both the position of atom '1' with respect to a chosen origin and to the directional dependence of the $r_{12}$ vector, it becomes impractical, because of the vast computing time involved, to recalculate the value of $B^{dd}$ by including $U^{dd}$ in $U(r_{12})$ of (4.21). However, the effect of the addition of $U^{dd}$ to the $U(r_{12})$ term may be determined, in particular, for the instance when the induced-induced dipole interaction will be a maximum, that is when one atom is at an ion position. The induced dipole will be perpendicular to the surface plane at the ion position but at other positions is generally dependent on the $x$ and $y$ components of the electric field. The following algorithm was used for the computation of $U^{dd}$ for the two atoms at positions $r_1$ and $r_2$ above the surface plane:

(i) The electric field components and induced dipoles were calculated at $r_1$ and $r_2$.

(ii) The origin of the coordinate system was translated from the cation position to the first atom position.

(iii) The $xy$ plane was rotated, firstly about the $z$-axis and secondly about the $y$ axis such that the $x$ axis lay along the $r_{12}$ vector.

(iv) From the concomitant operations on the field vectors, the angles $\phi_1$, $\phi_2$, $\theta_1$ and $\theta_2$ were determined by simple geometry without any ambiguity over the signs.

After testing the program by a number of hand calculations, it was used to determine $U^{dd}$ at $z^*_1 = z^*_2 = 0.56$, (the region where $U_g(r)$ is a minimum), with the first atom at $(0, 0, 0)$ and the second along the $y = 0$ and $x = y$ lines. The results shown in fig. 4.7 indicate that the $U^{dd}$ contribution to the inert gas self-interaction is small in comparison to $U(r_{12})$ in the region of the potential energy well, but does increase to the same order of magnitude as $U(r_{12})$ at $z^* = 1.9$. 


Fig. 4.7 Comparison of the argon self-interaction potentials as described in the text

Key: 
- , on the relaxed (100) surface
- , on the ideal (100) surface
As would be expected from the curves in fig. 4.7, the calculation of
the one-dimensional Mayer functions along the $y = 0$ and $y = x$
directions:

$$I = \int_{0}^{\infty} \exp \left\{ -\left[ U(r_{12}) + U^{dd}(r_{12}, r_{01}, \phi_{12}) \right] / \kappa \right\} - 1 \, dr_{12} \quad (4.80)$$

show that the contribution of $U^{dd}$ to the integral is less than 5%.
This percentage is likely to be less for the two-dimensional Mayer
function, $f_{12}$, because of the cancellation of the positive and
negative loops of the interaction terms when integrated over the
entire surface. In any case the error incurred through neglecting
the $U^{dd}$ term is likely to be less than that caused by the uncertainty
in the $U(r_{12})$ function itself. For this reason the induced dipole
interaction is not thought to be important in the present calculation.

### 4.8 THE TWO-DIMENSIONAL APPROXIMATION

The two-dimensional approximation was introduced in §4.4 through
the use of the first term in the Taylor expansion, (4.70), to derive
the two-dimensional second virial coefficient expressed in (4.71).
This approximation is equivalent to the assumption that the "out of
plane" interactions of the adsorbed gas atoms with each other can be
ignored i.e. when $z_{12} > 0$. Using (4.70) and (4.69) the sum of the
first corrections to $B_{2D}$ is:

$$G = \frac{-n_{1}^{2}}{\pi} \int_{0}^{\infty} \frac{e(0)}{e(z_{1}^{*})e(z_{2}^{*})f''(\theta, 0)(z_{1}^{*} - z_{2}^{*})^{2} \, dz_{1} \, dz_{2}}$$

with the integrals over the adsorption volume. $f''$ may be obtained
from the Bessel transform:
\[ f''(g_1 z_{12}) = \int_0^\infty f''(g, r_{12}) r_{12}^2 dr_{12} \]  

(4.82)

since \( J_0(g, r_{12}) \) is independent of \( z_{12} \). In the case of the generalized interatomic potential, \( U(r_{12}) = c_1 \exp(-c_2 r_{12}) - c/r_{12}^6 \), the second derivative of the Mayer function is:

\[ f''_{12} = \frac{1}{kT} \exp[-U(r_{12})/kT] \left\{ \frac{1}{kT} \left[ 6c r_{12}^{-7} + c_1 c_2 g \exp(-c_2 r_{12}) \right] r_{12}^2 \right\} - c_1 c_2 \]

\[ \exp(-c_2 r_{12}) \left[ c_2 g^2 - y - 6c r_{12}^{-7} \left[ y - 7 r_{12}^{-1} \right]^2 \right] \]  

(4.83)

where \( g = d r_{12} / dz_{12} \) and \( y = d^2 r_{12} / dz_{12}^2 \).

The function (4.83) shows the correct behaviour, (see fig. 4.8), as compared to the original Mayer function. By substituting (4.83) into (4.82) and evaluating at \( z_{12} = 0 \), the required transform is obtained:

\[ f''(g, 0) = \frac{1}{kT} \int_0^\infty \exp[-U(r_{12})/kT] \left\{ \frac{6 c_1 c_2}{r_{12}} \exp(-c_2 r_{12}) - 6 c r_{12}^{-8} \right\} \times \]

\[ J_0(g, r_{12}) r_{12}^2 dr_{12} \]  

(4.84)

This may be written in the reduced form:

\[ f''(g^+, 0) = \int_0^\infty \exp \left\{ \frac{-6}{T^+(a - \theta)} \exp[a(1 - \tau_{12}^+)] + \frac{1}{T^+(1 - 6/a)(\tau_{12}^+)^6} \right\} \]

\[ \left\{ \frac{6}{T^+(1 - 6/a)(\tau_{12}^+)^6} \exp[a(1 - \tau_{12}^+)] - \frac{6}{T^+(\tau_{12}^+)^6(1 - 6/a)} \right\} \]

\[ \times J_0(g^+, \tau_{12}^+) \tau_{12}^+ dr_{12} \]  

(4.85)

where \( g^+ = h r_m \tau_{12}^+ = \tau_{12} / r_m \) and \( T^+ = kT/\epsilon \).
Fig. 4.8 The evaluation of $f''_{12}$ and $f_{12}$ for argon at 77.5K
Fig. 4.9 Variation of $f''(n)$ with $T^+ (T^+ = kT/e)$ for the argon self-interaction potential.
Fig. 4.10 Convergence of Taylor's expansion used in the 2-D approximation
If \( f(g_{1\perp z_{12}}) \) is calculated by the Taylor's expansion (4.70) by using only the first correction term i.e. the second derivative term, the result is found to be in agreement with a direct evaluation of \( f(g_{z_{12}}) \) for \( g^+ = 0 \) and \( z_{12} < 0.3 \text{nm} \). This "out of plane" distance is the maximum likely in the present treatment since the total range of \( z \) in the integrals for \( \langle e_0 \rangle \) is generally only 0.3 nm. However in the cases of the \( n = 1 \) and \( n = 2 \) terms, the inclusion of the first correction is inadequate. For the \( n = 1 \) term at 77.5 K, substantial errors begin at \( z_{12} = 0.08 \text{nm} \), rising steeply to beyond 70% at \( z_{12} = 0.25 \text{nm} \) as shown in fig. 4.10a. A similar trend is also found for the \( n = 2 \) values (fig. 4.10b). The limits quoted above are also applicable at \( T^+ = 0.6 \) since the rate of convergence of the expansion (4.70) is not very sensitive to the temperature.

The sum of the second corrections to \( B_{2D} \) may also be expressed in a similar form to \( G \) of (4.81):

\[
F = \frac{\pi^4}{24} \int_{-\infty}^{\infty} e_{12}(z^+) e_{22}(z^+) (z^+ - z^2)^4 f^{iv}(g_{z12}) dz_1^2 dz_2^2 \\
\langle e_0 \rangle ^2
\]

After some lengthy algebra, (see Appendix 2), the fourth derivative transform may be written:

\[
f^{iv}(g^+,0) = - \int_0^{\infty} \exp \left\{ -(6q/a) \exp[a(1 - \tau_{12}^+)] + q(\tau^+)^{-6} \right\}
\]

\[
\left\{ 18p r_m^{-2} \left[ a(\tau_{12}^+)^{-1} + (\tau_{12}^+)^{-2} + 12q(\tau_{12}^+)^{-3} - 6p(\tau_{12}^+)^{-1} \right] -36q r_m^{-2} \right\}
\]

\[
\left[ 4(\tau_{12}^+)^{-9} + 3q(\tau_{12}^+)^{-15} \right] \times J_0(g^+,\tau_{12}^+) d\tau_{12}^+
\]

(4.87)
where \( q = \frac{a}{T'(\alpha - 6)} \) and \( p = q \exp[\alpha(1 - T^t_{12})] \)

The behaviour of \( f^i_{12} \) was compared to that expected from \( f_{12} \) and found to be in agreement.

The inclusion of the second correction term to the series (4.70) is found to bring the approximation closer to the direct calculation as shown in figs 4.10a and 4.10b. With the \( n = 1 \) term errors now begin at \( z_{12} = 0.15\text{nm} \) and rise slowly to 30\% at \( z_{12} = 0.25\text{nm} \). The computed values of \( f'' \) and \( f^{iv} \) are shown in Table 4.8.

**TABLE 4.8 VALUES OF THE SECOND AND FOURTH DERIVATIVES OF THE BESSEL TRANSFORM OF THE MAYER FUNCTION USED FOR THE "OUT OF PLANE" CORRECTIONS IN \( B_{2D} \)**

Units of \( f^{iv}(n,0) \) are \( 10^2 \text{nm}^{-2} \)

<table>
<thead>
<tr>
<th>n</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T^+ = { f''(n,0) } )</td>
<td>1.0002</td>
<td>-1.2163</td>
<td>-2.0813</td>
<td>2.4981</td>
<td>1.9692</td>
<td>-2.4699</td>
</tr>
<tr>
<td>( 0.4610 { f^{iv}(n,0) } )</td>
<td>( 3.1 \times 10^{-8} )</td>
<td>1.5894</td>
<td>-2.4567</td>
<td>-0.5317</td>
<td>3.9557</td>
<td>0.3337</td>
</tr>
<tr>
<td>( T^+ = { f''(n,0) } )</td>
<td>1.0001</td>
<td>-0.9218</td>
<td>-1.2641</td>
<td>1.5792</td>
<td>1.1726</td>
<td>-1.5045</td>
</tr>
<tr>
<td>( 0.60 { f^{iv}(n,0) } )</td>
<td>( 1.4 \times 10^{-8} )</td>
<td>0.9711</td>
<td>-1.6870</td>
<td>-0.1977</td>
<td>2.5596</td>
<td>0.1314</td>
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</tbody>
</table>

Using the expressions for \( f^{iv} \) and \( f'' \) it is now possible to compute the \( F \) and \( G \) terms contributing to \( B_{2D} \). This is a complex calculation because of the \( (z^*_1 - z^*_2)^2 \) and \( (z^*_1 - z^*_2)^4 \) terms. However it was carried out here on a computer by allowing the \( e_n(z^*) \) functions to be treated as numerical functions and values over a range of \( z^* \) were held in store. The evaluation of \( e_n(z^*) \) from this store was achieved by using the Everett central difference method of interpola-
The amount of the stored data was such that the interpolation was of the desired accuracy. The integral limits of \( z^* \) were the same as those used in §4.6 (0.46 < \( z^* \) < 1.0). Using the same integration methods as discussed previously, it was found that at the liquid nitrogen temperature only the \( n = 0 \) and \( n = 2 \) terms in (4.81) are large enough to be worth considering and these are smaller or of the same magnitude as the \( n > 10 \) terms ignored in the \( B_{2D} \) calculation.

The first three members in the summation \( G \) amount to a correction of \( 0.220 \times 10^{-20} \text{ m}^2 \text{ atom}^{-1} \) in \( B_{2D} \). If the fourth derivative correction, \( F \), is included, the total change becomes \( 0.334 \times 10^{-20} \text{ m}^2 \text{ atom}^{-1} \).

Although higher derivative correction terms would improve the accuracy, the magnitude of the correction is small and not a serious source of error in the present treatment. As indicated above, the magnitude of the correction for any system studied may easily be obtained from the second and fourth derivative terms in the Taylor's expansion of \( f(E,z_{12}) \).

### 4.9 HENRY'S LAW CONSTANT AND THE ISOSTERIC ENTHALPY OF ADSORPTION

The Fourier expansion of the potential field, \( U_s(r) \), can also be used to calculate properties that depend solely on the gas-solid interaction energy. Two of these properties, the isosteric enthalpy at zero coverage and the Henry's law constant, have been discussed in Chapter 3 in terms of the ht model and limiting models that assumed a perfectly mobile or completely localized adsorbed atom.

With the correct choice of the adsorption energy potential field, this calculation of \( q_{0}^{st} \) and \( K_{H} \) should be exact. Most of the computational methods developed for the calculation of the gas-solid perturbation terms to the two-dimensional second virial coefficient can be applied in the present calculation.
From (4.25) and (4.57)

\[ K_H = \frac{\pi}{kT} \int_0^\infty [e_0(z^*) - 1] dz^* \quad (4.88) \]

For the limiting isosteric enthalpy:

\[ q_{st}^0 = RT \left\{ \frac{\partial \ln P}{\partial T} \right\}_{n_a, A} \quad (4.89) \]

\[ \leftrightarrow = - \frac{RT^2}{K_H} \frac{dK_H}{dT} \quad (4.90) \]

giving the result:

\[ q_{st}^0 = RT - \frac{La}{kTK_H} \iiint \cos(g, r) \times \]

\[ U_s(r) \exp[-U_s(r)/kT] ds_1 ds_2 dz^* \quad (4.91) \]

where \( s_1 \) and \( s_2 \) are the reduced x and y coordinates. Since the adsorption volume approximation is not used in the evaluation of \( K_H \) (4.25), and hence \( q_{st}^0 \), the integral over \( z^* \) is taken over the container volume. However, as shown in fig. 4.11, the integrals quickly converge. As expected the integrand in (4.88), for \( z^* < 0.45 \), takes the value of -1.

The results of the computation of \( K_H \) and \( q_{st}^0 \) are shown in Table 4.9 for the three gas-solid potential functions listed in §4.3.5 and discussed in Chapter 2. The results in Table 4.9 confirm that the ht model is useful and capable of giving \( q_{st}^0 \) values to within 3% of the values derived from the Fourier expansion of \( U_s(r) \), and \( K_H \) values to within 10%. The values obtained using the ideal two-dimensional gas model show approximately 13% differences in \( q_{st}^0 \) and 100% or greater in \( K_H \). The results on the relaxed surface using
Fig. 4.11 Evaluation of $I^{st}$ required in the determination of $q_{0}^{st}$ and $I^{KH}$ used in the determination of $K_{H}$

\[ I^{st} = \int_{0}^{1} \int_{0}^{1} \cos(\gamma r) \exp(-U_{s}(r)/kT) \times U_{s}(r)/kT^{2} ds_{1} ds_{2} \]

\[ I^{KH} = e_{0}(z^*) - 1 \]

Key: • negative loop of $I^{KH}$
TABLE 4.9 COMPARISON OF $K_H$ AND $q_0^{st}$ VALUES AT 80K

(ht) - values derived using the hindered translation model; (ur) - values derived for the unrelaxed (100) surface; (r) - values derived for the relaxed (100) surface;

(a) Ross and Hinchen (1970); (b) Jackson and Davis (1974).

<table>
<thead>
<tr>
<th>gas-solid potential</th>
<th>$v_{\text{min}}^{ur}$ /kJ mol$^{-1}$</th>
<th>$K_H^{ur}$ /10$^{13}$ x atom N$^{-1}$</th>
<th>$K_H^{ht,ur}$ /10$^{13}$ x atom N$^{-1}$</th>
<th>$q_0^{st}(ur)$ /kJ mol$^{-1}$</th>
<th>$q_0^{st}(ht,ur)$ /kJ mol$^{-1}$</th>
<th>$q_0^{st}(ht,r)$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.519</td>
<td>1.65</td>
<td>1.73</td>
<td>4.08</td>
<td>4.17</td>
<td>4.48</td>
</tr>
<tr>
<td>B</td>
<td>0.659</td>
<td>5.40</td>
<td>5.38</td>
<td>4.96</td>
<td>5.11</td>
<td>5.31</td>
</tr>
<tr>
<td>C</td>
<td>1.023</td>
<td>103.9</td>
<td>112.5</td>
<td>7.21</td>
<td>7.33</td>
<td>7.62</td>
</tr>
<tr>
<td>experimental values</td>
<td></td>
<td></td>
<td></td>
<td>6.86$^{(a)}$</td>
<td>6.99$^{(b)}$</td>
<td></td>
</tr>
</tbody>
</table>
the potential parameters in the sets A, B and C show a systematic difference when compared with the values of the isosteric enthalpy on an ideal surface of the order of 4-8%, whereas the Henry's constant is more sensitive, with values for a relaxed surface of 2.02, 6.43 and 147.3 atom N\(^{-1}\) for the three cases. The isosteric enthalpy values observed experimentally are larger than those predicted by model A but in closer agreement with model C. If model B is used then the value of \(N\), the equivalent number of oscillators contributing to the polarizability of the atom, would need to be altered from that value of the corresponding inert gas core if agreement with the experiment is to be obtained. It would be expected that for a chloride ion \(N\) should increase from the value of 6.5 used for argon, and similarly for the sodium ion a decrease from 3.76 would be necessary, the value used for neon. It is found that the values of \(q^\text{st}_0\) and \(K_H\) for a relaxed surface are far less sensitive to changes in the cation dispersion constant compared to the anion. In this case a value of \(N\) of about 14 for the chloride ion in relaxed sodium chloride is required to give agreement with the experimental values of \(q^\text{st}_0\). A number of reasons can be postulated to explain this. Firstly the pairwise additive approximation has not been shown to be valid for this system, only that agreement between experimental and calculated values of \(K_H\) and \(q^\text{st}_0\) can be achieved within the limiting models for the gas-ion potential used in conjunction with the additive approximation. Secondly the values of the dispersion constants used in the most reliable of the models, model A, are obtained for the bulk ions. The electron distributions of the surface ions may be significantly perturbed from the bulk values resulting in larger dispersion interactions.
These results indicate that of the models used, model C should give the closest value to the experimental $B_{2D}$. Using the first five gas-solid perturbation terms yields a $B_{2D}$ value of $-17.9 \times 10^{-20} \text{ m}^2/\text{ atom}$ for argon on a relaxed (100) surface at 77.5K. This is considerably smaller than the $B_{2D}$ values previously calculated for model A. It is clear that further experimental evidence concerning $K_H$ and possibly $q_0^{st}$ is required to determine the $U_s(r)$ field to be used in the $B_{2D}$ calculation. Further to this, in spite of the three-body effect, the experimental values of $B_{2D}$ should clearly distinguish between the models adopted in the calculation.
Appendix 1

The Adsorption Volume Approximation

This approximation is concerned with writing the gas-solid
virial coefficients in terms of integrals over the adsorption volume,
$V_a$, rather than the total volume, $V$, i.e. the derivation of (4.29)
from (4.27).

Equation (4.17a) expresses the gas-solid virial coefficients:

\[ b_{AS} = z_1 - V \]  
\[ c_{AS} = z_2 - z_1^2 \]  
\[ d_{AS} = \frac{z_3}{2} - \frac{3z_1 z_2}{2} + z_1^3 \]

The configurational integrals $z_N$ are taken over the total volume $V$.
From the relationships stated in (4.16a) and (4.16b) it is possible
to write:

\[ z_1 - V = z_1^s \]  
\[ z_2 - z_1^2 = z_2^s - (z_1^s)^2 \]  
\[ z_3 - 3z_1 z_2 + 2z_1^3 = z_3^s - 3z_1^s z_2^s + 2(z_1^s)^3 \]

Also:

\[ z_1^s = \int_{V_a} \exp[-U(r_1)/(kT)] \, dr_1 + \int_{V_g} dr_1 - V \]

where the total volume is divided into a volume $V_a$ and bulk gas
volume $V_g$. When $U_s(r_1) >> kT$ then $V_a << V_g$ yielding:

\[ z_1^s = \int_{V_a} \exp[-U^*(r_1)/(kT)] \, dr_1 \]
and similarly:

\[ z_s^2 = \int \int \exp[-u^t(r_1, r_2) / kT] \, dr_1 \, dr_2 + 2(V_g - v) \int \exp[-u^t(r_1) / kT] \, dr_1 + (V_g - v)^2 \]  

(9)

\[ z_s^2 = \int \int \exp[-u^t(r_1, r_2) / kT] \, dr_1 \, dr_2 \]  

(10)

and similarly:

\[ z_s^3 = \int \int \int \exp[-u^t(r_1, r_2, r_3) / kT] \, dr_1 \, dr_2 \, dr_3 \]  

(11)

Hence \( z_s^1, z_s^2 \) and \( z_s^3 \) correspond to \( z_1, z_2 \) and \( z_3 \) but with the integrals over \( V_a \) rather than \( V \). If (4), (5) and (6) are substituted into (1), (2) and (3) and equations (8), (10) and (11) used, the evaluation of \( B_{AS}, C_{AAS}, D_{AAAS} \) yield the results in (4.29) and (4.30).

The magnitude of error resulting from this approximation may be obtained by examining (7). Neglecting the last two terms in (7) gives a relative error in \( B_{AS} \) of

\[ \delta = \frac{Az_u^* - Az_a^*}{Az_u^*} \frac{Az_u^*}{\int \exp[-u^t(r_1) / kT] \, dr_1} \]  

(12)

where \( z_u^* \) is the upper limit to the \( z \) coordinate of the volume \( V \) and \( z_a^* \) the thickness of the adsorption volume. Using the Fourier expansion (4.59) gives:

\[ \int \exp[-u^t(r_1) / kT] \, dr_1 = A_{e_0}^< > \]  

(13)

hence:

\[ \delta = \frac{z_u^*}{<e_0^< >} \]  

(14)
For argon on ideal sodium chloride at 77.5 K, $z^*_a = 1$ and $<e_0> = 43.17$ thus introducing an error of about 2% in $B_{AS}$.

Steele (1973b) has presented values of $<e_0>$ for adsorption at high $T^+$ values on a monatomic f.c.c. lattice as low as 1.84 which indicate that the adsorption volume approximation is no longer valid for this case because the final two terms in (7) are no longer small compared to the first.
APPENDIX 2

THE DETERMINATION OF \( \tau_{12}^{iv} \) FOR THE "EXP6" EQUATION

The Mayer function of (4.21) may be differentiated twice w.r.t. \( z \) to obtain:

\[
\tau_{12}^{iv} = -\frac{D}{kT} \left[ B^{'''} + \frac{(B^2)''}{kT} - \frac{2BB'' + (B')^2}{kT} + \frac{(B^3)'}{(kT)^2} \right]
\]

\[
\tau_{12}^{iv} = -\frac{D'}{kT} \left[ B'' - \frac{(B^2)'}{kT} - \frac{BB'}{kT} + \frac{B^3}{(kT)^2} \right]
\]

where

\[ D = \exp(-U/kT) \]  \hspace{1cm} (2)

\[ B = \frac{3U}{3z_{12}} \]  \hspace{1cm} (3)

hence

\[ D' = -\frac{1}{kT} BD \]  \hspace{1cm} (4)

Since at \( z_{12} = 0, B = 0 \) equation (1) becomes:

\[
\tau_{12}^{iv} = -\frac{D}{kT} \left[ B^{'''} - \frac{1}{kT}(B^2)'' - \frac{(B')^2}{kT} + \frac{(B^3)'}{(kT)^2} \right]
\]

The terms in (5) may be evaluated by writing

\[ B = -c_1c_2g \exp(-c_2z_{12}) + 6Cr_{12}^{-7}g \]  \hspace{1cm} (6)

where

\[ g = z_{12}^{2}(\tau_{12}^{iv} + z_{12}^{2})^{-\frac{1}{2}} \]  \hspace{1cm} (7)

The values of the various derivatives of \( g \) at \( z_{12} = 0 \) that are required to evaluate (5) are summarized in Table 1.
TABLE 1 VALUES OF THE DERIVATIVES OF g AT z_{12} = 0

<table>
<thead>
<tr>
<th>term</th>
<th>value at z_{12} = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>g'</td>
<td>\tau_{12}^{-1}</td>
</tr>
<tr>
<td>g''</td>
<td>0</td>
</tr>
<tr>
<td>(g^2)'</td>
<td>0</td>
</tr>
<tr>
<td>(g^3)'</td>
<td>0</td>
</tr>
<tr>
<td>(g^2)''</td>
<td>2\tau_{12}^{-2}</td>
</tr>
<tr>
<td>g'''</td>
<td>-3\tau_{12}^{-3}</td>
</tr>
</tbody>
</table>

The resulting equations for the terms in (5) at z_{12} = 0, are listed below:

\[ B'' = 3c_1c_2^2\tau_{12}^-2\exp(-c_2\tau_{12}) + 3c_1c_2^3\tau_{12}^-3\exp(-c_2\tau_{12}) - 14t_{12}^-10 \]  
\[ (B^2)'' = 2c_1c_2^2\tau_{12}^-2\exp(-2c_2\tau_{12}) + 72c_1c_2\tau_{12}^-16 - 24c_1c_2\tau_{12}^-2\exp(-c_2\tau_{12}) \]  
\[ (B')^2 = -12c_1^2c_2\tau_{12}^-9\exp(-c_2\tau_{12}) + c_1^2c_2^2\tau_{12}^-2\exp(-2c_2\tau_{12}) + 3c_1^2\tau_{12}^-16 \]  
\[ (B^3)'' = 0 \]  

Collecting terms gives:

\[ \left(\sigma_{12}^{iv}\right)_{z_{12} = 0} = -\exp(-U/kT) \left[ \frac{3c_1c_2^2\tau_{12}^-2\exp(-c_2\tau)}{kT} \right] + \frac{3c_1c_2\tau_{12}^-3\exp(-c_2\tau)}{kT} - \frac{14\tau_{12}^-10}{kT} - \frac{3c_1c_2^2\tau_{12}^-2}{(kT)^2} \times \]
Equation (12) can now easily be used to obtain the reduced form of \( f^{iv}(g,0) \) shown in (4.87).
5.1 INTRODUCTION

The adsorption potential field experienced by a gas atom above a surface will exhibit some form of heterogeneity due to the surface structure. This may be of an intrinsic type that has been discussed in Chapter 3 and 4, or it may be a more general and less defined residual type of heterogeneity. This residual heterogeneity, subsequently referred to as the heterogeneity, may be ascribed to defects in the surface, impurities on or in the surface, corners, edges, kinks and steps on crystal faces, the internal pore structure of the solid or simply the existence of many different exposed crystal faces. Although attempts to measure this heterogeneity using multilayer adsorption theory have been made, (Halsey 1951), difficulties arise in distinguishing monolayer sites of low energy from multilayer sites, and the exact form of the decrease in adsorption energy with multilayer formation.

When analysing experimental isotherms, the degree of heterogeneity of the surface is very important if meaningful results are to be obtained. Many of the classical equations that have been widely used in the past years to analyse experimental results, are strictly applicable to homogeneous surfaces. These equations include the Langmuir and the Hill-de Boer equation. A completely rigorous approach would require detailed information about the nature and spatial distribution of the heterogeneities so that the lateral interactions of the adsorbed molecules could be determined.
To overcome this problem two models have been suggested. The random surface model (Hill 1949, Steele 1963) has been investigated but remains impractical and intuitively unrealistic since for most surfaces a completely random distribution of sites is not expected. The patchwise model, (Ross and Olivier 1964), has been more successful. In this approach the heterogeneity is described by a number of patches of different adsorption energy. In practice this distribution of patches can be continuous. The major assumption implicit in this model is that only lateral interactions within a particular energy patch can be accounted for and that the patches are large enough so that edge effects, i.e. lateral interactions between patches, are negligible.

Using the patchwise model the integral equation for the adsorption isotherm on a heterogeneous surface is of the general form:

$$
\theta = \int_0^\infty \phi(U) \psi(P, U) dU
$$

where:

- $\theta$ is the fractional monolayer coverage of the surface, i.e.
- $\theta = \frac{n_a}{n_m}$ where $n_a$ is the number of atoms adsorbed and $n_m$ is the number of atoms adsorbed at the point of monolayer coverage.
- $\phi(U)$ is the distribution function of the adsorption energy. $U$ is the maximum adsorption energy, $U^0$, minus the zero state vibrational energy and is taken as positive in magnitude. ($U$ corresponds to $U_0$ used by Ross and Olivier (1964) and House and Jaycock (1974a); similarly, $U^0$ corresponds to $g_{ads}$).
- $\psi(P, U)$ is the model isotherm function discussed below.

5.2 THE MODEL ISOTHERM FUNCTIONS

5.2.1 The Hill-de Boer Function

In this treatment the bulk phase gas above the solid is in equi-
equilibrium with an adsorbed phase. The characteristic parameters for the adsorbed phase can be obtained by the application of classical statistical mechanics. One approach is to represent the adsorbed phase as an ensemble of \( n_a \) gas atoms, each atom having two degrees of translational freedom and a third degree of vibrational freedom perpendicular to the surface. The reference or zero state is taken as an isolated gas atom at rest. The finite size of the adsorbed atoms and the potential energy between adsorbed atoms is approximated as in the three-dimensional van der Waals equation of state.

For a mass point moving in an area \( A \) with two degrees of translational freedom, the partition function is:

\[
f = \frac{2\pi nkTA}{\hbar^2}
\]  

(5.2)

A "free area", \( A_f \), may be introduced such that:

\[
A_f = A - n_a \beta
\]  

(5.3)

where the excluded area \( \beta = \pi r_m^2 / 2 \); \( r_m \) is the interatomic separation at the minimum in the adsorbate self-interaction potential. The potential energy between the two atoms takes the form:

\[
U(r) = \begin{cases}  
\varepsilon (r_m/r)^6 & \text{for } r > r_m \\
\pm \infty & \text{for } r \leq r_m 
\end{cases}
\]  

(5.4)

where \( r \) is the interatomic separation. The mutual interaction of one atom with surrounding atoms may be calculated, assuming a uniform density \( n_a / A \). Within a distance \( r \) to \( r + dr \) there are \( n_a 2\pi r/\hbar \) atoms and so a total interaction energy:

\[
w = - \int_{r_m}^{\infty} \varepsilon (r_m/r)^6 \frac{n_a}{\hbar} 2\pi r dr
\]  

(5.5)
hence \( w = -2\alpha n_a / A \) where \( \alpha = \varepsilon \pi r_m^2 / 4 \)

The total partition function for this system of indistinguishable atoms becomes:

\[
Q = \left[ \frac{2\pi mkT}{\hbar^2} A_f \exp(-w/2kT) \right]^{n_a / n_a} (5.6)
\]

If the internal substructure, i.e. electronic and nuclear energies, is accounted for by using a partition function \( f_a \) and the vibrational degree of freedom is separated with a corresponding partition function \( f_z \), the total partition function for the adsorbed phase is:

\[
Q = f_a^n (A - n_a \beta) \exp(n^2_a / AkT) n_a! (5.7)
\]

where \( f = f_a f_z 2\pi kmT h^2 \exp(U/kT) \)

The chemical potential of the bulk gas is:

\[
\mu = \mu^0 + kT \ln P \quad (5.8)
\]

where \( \mu^0(T) = -kT \ln \left[ \frac{2\pi mkT}{\hbar^3} \right]^{3/2} \frac{kTf_g}{g} \quad (5.9) \)

and \( f_g \) is the internal substructure partition function of the bulk gas. At equilibrium the chemical potential of the bulk gas and the adsorbed phase are equal and so the pressure becomes:

\[
P = \exp \left[ \frac{\partial F}{\partial n_a} \right]_{A, T} / kT - \mu^0(T) / kT \quad (5.10)
\]

where \( F \) is the Available energy or Helmholtz function for the adsorbed phase obtained from \( Q \) in (5.7). It is reasonable to assume that \( f_g = f_a \) so that:
\[ P = K \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta} - \frac{2\alpha \theta}{\beta kT}\right) \]  
(5.11)

where
\[ K = \left(\frac{\beta \mu N kT}{h^2}\right)^{\frac{1}{3}} \frac{kT}{\beta \mu Z} \exp\left(-\frac{U}{kT}\right) \]  
(5.12)

\[ \theta = \beta n_A / A \]

and
\[ f_z = \left[1 - \exp(-h\nu/kT)\right]^{-1} \]  
(5.13)

Since \( U \) is used in (5.7) instead of \( U^0 \), the ground state vibrational energy is now included in \( U \) yielding (5.13).

Equation (5.11) is in the generalized form for the model isotherm function:
\[ P = Kg(\theta,T) \]  
(5.14)

where \( K \) is written in the generalized form:
\[ K = A^0 \exp(-\frac{U}{kT}) \]  
(5.15)

(5.11) is referred to as the Hill-de Boer equation (HdB). It is mathematically simple, but still predicts critical and phase transition behaviour.

The critical point can be determined from
\[ \frac{d^2 g(\theta,T)}{d\theta^2} = 0 = (V' - C)(V' + V'' - VC) + [V'' + V'' + (V')^2 - CV'] \]
(5.16)

where \( V = 1/\phi, \ V' = 1/\phi^2, \ V'' = 2/\phi^3, \ \phi = 1 - \theta \) and \( C = \frac{2\alpha}{kT} \).

To solve (5.16) analytically a further constraint is required:
\[ \frac{dg(\theta,T)}{d\theta} = 0 \]

Using this method the critical point is found to occur at \( C = 6.75, \ \theta = 0.3333^r \) and \( P/K = 0.08688697 \). Below the critical point
there are three roots to (5.16) because of the characteristic loop. Since the stable equilibrium path of the phase transition is required, the thermodynamic equal-area theorem of the log P/K vs. θ plot, (de Boer and Broekhoff 1967), is used to determine the upper coverage value, θ_h, and the lower coverage value, θ_l, of the phase transition at a particular value of P/K. For convenience these values are reproduced from the work of Waldsax (1970) in Table 5.1.

Above the critical point dg(θ,T)dθ ≠ 0 at the inflection point. However (5.16) has a unique solution that can be determined numerically. An iterative "half-step" method was used to solve (5.16) to a relative accuracy of 10^-9. These values are shown in Table 5.2.

Once the values of C and K are known for a particular system, the HdB function (5.11) may be characterized for any homotattic patch of energy U.

The value of C may be obtained by evaluating α and β from the corresponding 'a' and 'b' values in the van der Waals equation.

\[ α = a(9π/256b)^{1/3} \quad \text{and} \quad β = 2b(9π/256b)^{1/3} \]  
\[ \frac{α}{β} = \frac{a}{2b} \]  
\[ \text{so that} \quad \frac{α}{β} = \frac{a}{2b} \]

A number of uncertainties do exist in the evaluation of C. Firstly the 'a' and 'b' constants are usually determined from the experimental values of the critical temperature and volume, T_c and V_c, of the gas. If the Boyle properties, T_B and V_B (Munn 1964), are used different values of 'a' and 'b' are obtained. This is shown for argon at 77.5K when using the critical parameters to determine α and β, C = 6.52 compared to C = 5.29 obtained using the Boyle properties. Secondly the perturbation of the adsorbate by the substrate could have serious effects on the values of α and β. Orientation of the adsorbed molecule by the surface potential field will be important


TABLE 5.1 THE HILL-DE BOER PHASE TRANSITION PARAMETERS

\[ C = \frac{2a}{kT} \], \( \theta_\perp \) and \( \theta_h \) are the lower and higher coverages at a step position \( P/K \) (eqtn. 5.11)

<table>
<thead>
<tr>
<th>( C )</th>
<th>( \theta_\perp )</th>
<th>( \theta_h )</th>
<th>( P/K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.035848166</td>
<td>0.728671030</td>
<td>0.026963881</td>
</tr>
<tr>
<td>9.9</td>
<td>0.037627059</td>
<td>0.724596920</td>
<td>0.028012955</td>
</tr>
<tr>
<td>9.8</td>
<td>0.039505311</td>
<td>0.720387470</td>
<td>0.029099472</td>
</tr>
<tr>
<td>9.7</td>
<td>0.041489699</td>
<td>0.716035140</td>
<td>0.030224587</td>
</tr>
<tr>
<td>9.6</td>
<td>0.043587603</td>
<td>0.711531810</td>
<td>0.031389451</td>
</tr>
<tr>
<td>9.5</td>
<td>0.045807084</td>
<td>0.706868630</td>
<td>0.032595261</td>
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<td>0.279353000</td>
<td>0.366835861</td>
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</tr>
</tbody>
</table>
### Table 5.2: The Hill–de Boer Inflection Point Parameters

\[
C = 2a/kT, \quad \theta_i, \text{ and } P/K \text{ locate the inflection point}
\]

<table>
<thead>
<tr>
<th>C</th>
<th>(\theta_i)</th>
<th>(P/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.75</td>
<td>0.3333333</td>
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</tr>
<tr>
<td>6.70</td>
<td>0.3333059</td>
<td>0.08834710</td>
</tr>
<tr>
<td>6.60</td>
<td>0.3330865</td>
<td>0.09133838</td>
</tr>
<tr>
<td>6.50</td>
<td>0.3326481</td>
<td>0.09442162</td>
</tr>
<tr>
<td>6.4</td>
<td>0.3319911</td>
<td>0.09759292</td>
</tr>
<tr>
<td>6.3</td>
<td>0.3311164</td>
<td>0.1008476</td>
</tr>
<tr>
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</tr>
<tr>
<td>6.0</td>
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<tr>
<td>5.9</td>
<td>0.3254513</td>
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<td>5.8</td>
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<tr>
<td>5.7</td>
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<td>0.1217499</td>
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<tr>
<td>5.6</td>
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<td>5.5</td>
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<tr>
<td>4.5</td>
<td>0.2774049</td>
<td>0.1617357</td>
</tr>
</tbody>
</table>
for asymmetric polyatomic molecules and so affect the values of both α and β. In the case of inert gas atoms on ionic surfaces the major perturbation will be caused by the surface electric field. The induced dipoles that are formed, produce mutual repulsions and attractions that affect the value of α. de Boer (1950) has expressed the reduction:

$$\Delta a = \omega^2 \pi^{3/2} / \sqrt{2a}$$

(5.19)

where $\mu$ is the induced dipole moment of the adsorbed atom. An idea of the magnitude of this perturbation based on (5.19) may be obtained for the cases of argon and krypton adsorbed on relaxed sodium chloride:

(i) argon/NaCl (relaxed). The minimum potential energy site is at a distance 3.12 Å above the surface plane. At this position the atom has a dipole moment of $1.76 \times 10^{-18}$ e.s.u. and using a β value of $13.6 \times 10^{-16}$ cm$^2$ atom$^{-1}$ gives rise to $\Delta a = 1.88 \times 10^{-30}$ erg cm$^2$ atom$^{-2}$ which is a 3.97% change in α.

(ii) krypton/NaCl (relaxed). The minimum is at a distance of 3.33 Å from the surface. The dipole moment and β values are $2.95 \times 10^{-18}$ e.s.u. and $15.7 \times 10^{-16}$ cm$^2$ atom$^{-1}$ respectively. The corresponding $\Delta a = 2.95 \times 10^{-30}$ erg cm$^2$ atom$^{-2}$ which makes a 3.88% change in α.

Although some small perturbation effect on β is expected, it is difficult to account for this quantitatively. Unless otherwise stated the values of α and β are taken here from Ross and Olivier (1964). The values for argon and krypton respectively are 47.4, 76.0 $\times 10^{-30}$ ergs cm$^2$ atom$^{-2}$ and 13.6, 15.7 $\times 10^{-16}$ cm$^2$ atom$^{-1}$.

If K is known, $\ln A^0$ may be used to obtain U. From (5.12):

$$\ln A^0 = \ln \left[ \frac{2\pi mkT}{h^2} \right] + \ln \left[ 1 - \exp(-h\nu/kT) \right]$$

(5.20)
In this evaluation the units of $A^0$ must be those of the pressure in (5.14). The second term on the right of (5.20) is usually small at low temperatures and can be omitted. In the case of krypton on (100) sodium chloride at 77.5K, $v^t$ may lie between 0.75 to $1.06 \times 10^{12} \text{s}^{-1}$ yielding errors in $\ln A^0$ of 7.2% and 5.2% respectively. In cases when $v^t$ reaches $10^{13} \text{s}^{-1}$ the error is only 0.014%. For argon the situation is similar with errors of between 3.9 to 5.1%.

Another expression of $\ln A^0$ at low temperatures has been presented by Ross and Olivier (1964).

$$\ln A^0 = \ln M + \ln T - 0.5 + \ln 760 - \ln \left( \frac{1}{1 - \theta_s} \right) + 2.279/R \quad (5.21)$$

where the standard state coverage $\theta_s = \beta/4.08T$ and $M$ is the atomic weight of the gas. The adsorbed phase standard state was defined by de Boer and Kruyer (1952) such that the average interatomic separation would be the same as the bulk gas at 0°C.

Equations (5.20) and (5.21) give almost identical values of $\ln A^0$ in this work. However it has been noted by Hoory and Prausnitz (1967) that using (5.21), $U$ becomes dependent on the standard state chosen which is not consistent with the original definition of $U$ (Ross and Olivier 1964).

5.2.2 The Langmuir Function

The derivation of the Langmuir equation is well known (Hill 1960). Written in the form of (5.14)

$$g(\theta, T) = \theta/(1 - \theta) \quad (5.22)$$

$$K = \prod_i \left( 1 - \exp\left(-\frac{h v_i}{k T}\right) \right) \exp\left(-\frac{\mu_i^0}{k T}\right) \exp\left(-\frac{U}{k T}\right) \quad (5.23)$$

where the subscript $i$ refers to the three separate degrees of
vibrational freedom of the localized atom and $\mu_0^0(T)$ is related to (5.9) through

$$\mu_0^0 = \mu^0 + \ln f_g$$  \hspace{1cm} (5.24)

Using the low temperature approximation

$$\ln A^0 = \ln \left[ \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} kT \right]$$ \hspace{1cm} (5.25)

This is only an approximate expression. For example krypton at 77.5 K on sodium chloride, (5.25) may be in error by about 12% because of the vibrational frequency dependent terms in (5.23).

The same method used by Ross and Olivier for the HdB function may be adopted for the Langmuir equation. This yields a low temperature limit of:

$$\ln A^0 = (3R/2T)\ln N + (5R/2T)\ln T - 2.316/T - 5/2 + \ln 760 + \ln \theta_s$$

$$- \left[ (1 - \theta_s)/\theta_s \right] \ln (1 - \theta_s) \hspace{1cm} (5.26)$$

The loss of the frequency dependent terms also leads to errors of the magnitude associated with (5.25).

5.2.3 The Fowler-Guggenheim Function

As with the Langmuir function the Fowler-Guggenheim (FG) function is based on a localized model but includes average nearest neighbour interactions. This is handled on the basis of a random distribution of atoms among the sites. The methods used in §5.2.1 are applicable and yield:

$$K = \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} \frac{kT}{f_x f_y f_z} \exp(-U/kT) \hspace{1cm} (5.27)$$

where $f_x$, $f_y$ and $f_z$ are the partition functions for the degrees of freedom.
The isotherm equation becomes:

\[ F = K \frac{\theta}{1 - \theta} \exp(-Zw\theta/kT) \]  \hspace{1cm} (5.28)

where \( \omega \) is the nearest neighbour interaction energy and \( Z \theta \) is the number of occupied nearest neighbour sites.

The FG equation also exhibits the characteristic phase transition loop when \( \frac{Z\omega}{kT} \gg 1 \). The values of \( \theta_L \) and \( \theta_H \) below the critical temperature may be obtained from the symmetry condition:

\[ \theta_L = 1 - \theta_H \]  \hspace{1cm} (5.29)

with the corresponding \( P/K \) step value obtained from substituting \( \theta = 0.5 \) into (5.28). The \( \theta_L \) and \( \theta_H \) values may then be obtained by an "half-step" iterative procedure using (5.28). Above the critical point \( \theta_i = \frac{1}{2} \).

The main problems with the use of the FG function have been the determination of \( f_x, f_y, f_z \) and \( Z\omega \). Since generally:

\[ f_i = [1 - \exp(-\nu_i/kT)]^{-1} \]  \hspace{1cm} (5.30)

the low temperature approximation can be made as in §5.2.2. Alternatively the adsorbed atom can be thought of as confined to a limiting area on the surface, ("site area"), with two degrees of translational freedom. In this case:

\[ K = (2\pi mkT)^{\frac{3}{2}} \frac{kT}{\sigma f_z} \exp(-U/kT) \]  \hspace{1cm} (5.31)

where \( \sigma \) is the limiting site area. Using the low temperature approximation or knowing the magnitude of \( \nu^\perp \), the value of \( \ln A^0 \) may be determined.
The value of \( Z_w \) is usually taken as a fraction of the corresponding heat of vaporization or liquifaction of the bulk gas.

5.3 THE METHOD OF ROSS AND OLIVIER

This treatment for the determination of \( \phi(U) \) was proposed by Ross and Olivier (1964). The method uses the HdB function and a graphical technique to choose parameters that specify a Gaussian distribution of site energies. Since the analysis has been examined by Waldsax (1970), the details of the method will not be presented here.

It is a useful method that suffers a number of limitations which include:

(i) The \( \phi(U) \) is limited to a Gaussian function or some combination. The number of variables in the analysis increases with the number of separate Gaussian functions that are required and so the uncertainty in the choice of functions increases.

(ii) At the moment only tables for the HdB model are available.

(iii) The method is graphical and time consuming. Although the procedure could be computerized, the limitation imposed by (i) does not make it worthwhile.

5.4 ADSEFF: ALGORITHM FOR THE DETERMINATION OF SITE ENERGY FREQUENCY FUNCTIONS

5.4.1 Basis of the Algorithm

Equation (5.1) may be rewritten in the form:

\[
\frac{V_i}{V_m} = \int_{U_h}^{U_r} \frac{d\rho(U)}{dU} \psi(p_i, U) dU
\]  

(5.32)

where the subscript \( i \) labels a number of points, \( N \), characterizing the isotherm, \( U_h \) and \( U_r \), to be discussed later, are the adsorption energy limits imposed by the range of data and the model isotherm
function; \( F(U) \) is a numerical function of the fraction of the surface with energies \( U \) or less, and \( V_m \) may be considered for the present as the monolayer volume (cm\(^2\) g\(^{-1}\) at STP) or amount adsorbed with \( V_i \) in the same units. In more precise terms \( V_m \) is the adsorption that is required to normalize the distribution function through the iterative correction (ii) below. The problem is to get the root mean square (r.m.s.) deviation from the experimental data to a minimum.

\[
\text{rms} = \left( \frac{1}{N} \sum_{i=1}^{N} \left( \frac{V_i}{V_m} \right)^2 \right)^{1/2}
\]

(5.33)

This is done by changing the function \( F \) in two stages:

\[
\begin{align*}
(i) \quad F_i^{\text{new}} &= F_i^{\text{old}} \left( \frac{V_i/V_m}{\theta_{h}^{\text{old}}} \right)^{1/2} \left( \frac{P_{i}}{P_{N}} \right) \\
(ii) \quad V_m^{\text{new}} &= V_m^{\text{old}} \times P_N \\
F_i^{\text{new}} &= \frac{F_i^{\text{old}}}{P_N}
\end{align*}
\]

(5.34)

(5.35)

where the superscripts "new" and "old" indicate the improved and previous values respectively. The values of \( \theta_h \) and \( \theta_A \) are determined from (5.14) using the limiting values of \( P \). In this method all of the \( F_i \) values are changed after each iteration to obtain a new set of \( F_i \) values. These are used in subsequent evaluations of (5.33) as the new set of \( F_i \) values with the new \( V_m \) from (5.35) until the r.m.s. reaches a minimum.
For a rapid convergence using this procedure, the choice of the initial $F$ function is important. The method of Adamson and Ling (1961) chooses a monolayer adsorption from a BET analysis, and determines the first approximation to $F$ through

$$F_i = V_i/V_{\text{m(BET)}} \tag{5.36}$$

The use of (5.36) suffers from the disadvantage that $V_{\text{m(BET)}}$ is not always known or reliable and that the subsequent distribution function, $dP/dU$, is not normalized i.e. $F_{\text{N}} \neq 1$. Instead the initial approximation adopted here is

$$F_i = V_i/V_N \tag{5.37}$$

with

$$V_{\text{m}} = V_N.$$  

Subsequent iterations follow the procedure of (5.34) and (5.35) until the r.m.s. minimum is reached.

The adsorption energy limits and intervals are determined from the model isotherm function. Below the critical point a step does exist in the HdB and FG functions and the approximation used is:

$$K_i = P_i(K/P)_{\text{step}} \tag{5.38}$$

where the $(K/P)_{\text{step}}$ values are obtained from Table (5.1), and from (5.15)

$$U_i = kT(lnA - lnK_i) \tag{5.39}$$

(5.38) and (5.39) set the range of $K$ and $U$ used to determine the distribution function. Normally if $F_i < 0.1$, the distribution function is independent of the upper limit of $U$ determined by the lowest pressure measurements. (This is discussed further in §5.4.4.) If multilayer data is included, the normalizing factor $V_{\text{m}}$ will no longer correspond to the true monolayer capacity. $V_{\text{m}}$ can only be equal to the monolayer capacity if there is a distinct minimum in the frequency.
function at the lowest $U$.

A multilayer correction, $v_i^{\text{new}} = v_i^{\text{old}} \times (1 - P/P_0)$ where $P_0$ is the saturation vapour pressure of the adsorbate, may be applied. This has been used by Adamson and Ling (1961) but is a rather arbitrary choice, without clear theoretical foundations.

If there are adsorption sites of higher energy than the maximum $U$, they are assumed to fill according to a linear extrapolation of the measured isotherm to the origin. In the low pressure limit this corresponds to a Henry's law isotherm. Sites of energy less than the minimum, $U_m$, are assumed to be empty.

If the adsorption temperature is such that the model function does not exhibit a step or is the Langmuir function, the step is taken arbitrarily through the point of inflection (listed in Table 5.2 for the HdB function).

ADSEFF is the title of a computer program that was developed in this work to perform the computation of $\phi(U)$. This is a completely revised version of a former program that was previously used in the analysis of krypton adsorbed on anatase (House and Jaycock 1974a). The former program suffered a number of difficulties that were removed when rewriting. Facilities to smooth the input data were made so that the final distribution function did not include effects resulting from inherent experimental inaccuracies. The functions $F(K)$ and $F(U)$ were represented by cubic splines to be discussed in detail in §5.4.3, and all interpolations and subsequent first derivatives were obtained by using these spline fits. The accuracy of the individual numerical integrations was improved considerably. The final $dF/dU$ function was output directly from the program rather than the $F(U)$ function.

ADSEFF is written in Fortran IVD and requires a core space of 16k words. Although the program was run on a 1904A ICL computer, ADSEFF
is machine independent. It requires a minimum of computer time, taking on average about 7 minutes to perform 20 cycles on the ICL machine. The entire program consists of a control segment and 14 subroutines. It is capable of using the HdB, FG or the Langmuir equations as the model isotherm. Table 5.3 lists the subroutine names and brief details of their function. Appendix 3 presents a listing of ADSEFF.

<table>
<thead>
<tr>
<th>name of routine</th>
<th>purpose of routine</th>
</tr>
</thead>
<tbody>
<tr>
<td>MASTER</td>
<td>Controls input, the cycling and iterative improvements together with determining the final dF/dU function</td>
</tr>
<tr>
<td>DATASET</td>
<td>Optional; raw data is smoothed twice and new derived data points output on a logarithmic pressure scale</td>
</tr>
<tr>
<td>CORRECT</td>
<td>Optional; this routine may be called from DATASET to apply a multilayer correction</td>
</tr>
<tr>
<td>FEED</td>
<td>Determines whether all important stored information is to be output to routine SUPERDUCE</td>
</tr>
<tr>
<td>MONIT</td>
<td>Outputs pressure/volume and U/F values</td>
</tr>
<tr>
<td>CALC</td>
<td>Calculates the $\theta$ value for any model isotherm given the corresponding $P/K$ value</td>
</tr>
<tr>
<td>FUN</td>
<td>Calculates $P/K$ given a $\theta$ value</td>
</tr>
<tr>
<td>DEDT</td>
<td>$\theta$ value is input and the current $P_i$ is in a COMMON block; this routine determines the corresponding $K$ and $F$ values for the determination of the $\int_{\theta}^{0} F d\theta$ integral</td>
</tr>
</tbody>
</table>

TABLE 5.3 SUBROUTINES AND FUNCTIONS USED IN ADSEFF
TABLE 5.3 SUBROUTINES AND FUNCTIONS USED IN ADSEFF (Continued)

<table>
<thead>
<tr>
<th>name of routine</th>
<th>purpose of routine</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPLINC</td>
<td>Determines the spline coefficients for two one-dimensional input arrays of length ≤ 80</td>
</tr>
<tr>
<td>EVALUT</td>
<td>Interpolates using the cubic spline coefficients that are output from SPLINC</td>
</tr>
<tr>
<td>FQUAD</td>
<td>Determines the $\int_{\theta_2}^{\theta_1} P_1 , F d\theta$ integrals</td>
</tr>
<tr>
<td>SMOOTH</td>
<td>Optional; uses a 5 point quadratic smoothing procedure on two arrays input of dimension ≤ 80</td>
</tr>
<tr>
<td>COEF</td>
<td>This routine is called from SMOOTH to determine the least squares quadratic coefficients</td>
</tr>
<tr>
<td>GAUSSELIM</td>
<td>This is called from COEF to solve the least squares matrix for the quadratic coefficients</td>
</tr>
<tr>
<td>SUPERDUCE</td>
<td>Routine to output results if either maximum iterations are reached or the r.m.s. has reached a minimum. FEED may also activate SUPERDUCE</td>
</tr>
</tbody>
</table>

The skeleton structure of the master control segment which uses these 14 routines is shown in fig. 5.1.
FIG. 5.1 The Structure of the Control Segment of ADSEFF

ENTRY

read P, V and model isotherm parameters

call MONIT

do you require DATASET?

No

give you require DATASET?

Yes

initialize \( V_m \), \( F \), \( K \), \( \theta_{\text{expt}} \), \( U \)

is this the first cycle?

No

If this is the first cycle?

Yes

invert \( K \) to form \( A \)

\( \text{"F" "B} \)

\( \text{"U" "C} \)

read \( F \)

loop \( i = 1, N \)

call SPLINC for arrays \( A, B \)

call FQUAD to determine

\( \frac{\partial \theta_L}{\partial F} \) using DETD

\( \theta_L \)

\( \theta_h \)
FIG. 5.1 continued

1. apply iterative improvement (i)  →  $P_N > 1.0 \pm 10^{-4}$  →  Yes  →  apply iterative improvement (ii)
   No →

2. Yes →

3. is rms increasing?  →  $\theta^{\exp} = \theta^{\exp}/P_N$
   No →

4. is SMOOTH required?  →  Yes  →  call SMOOTH for arrays K, F
   No  →  No →

5. call SUPERDUCE
   →

6. call SPLINC for array C, B
   →

7. are maximum iterations reached?  →  Yes →  4
   No  →  4
FIG. 5.1 continued

U interval set for the determination of \( \frac{dF}{dU} \)

Loop \( i = 1, 80 \)

Call EVALUT to determine \( \frac{dF}{dU} \)

Calculate \( \frac{dF}{dU} \) by the direct gradient method

Are more iterations required?

Do you require card punch?

Output final \( F \) on cards

Stop
5.4.2 Least Squares Smoothing

The SMOOTH routine uses a composite formula to fit least square quadratics locally. The general method may use an ith degree polynomial with composite smoothing over a number of points greater than i. In this work quadratic polynomials are used to smooth over an odd number of consecutive points at a time. The method consists of fitting successive least square quadratics over n points, finally fixed at 5, and obtaining one smooth value at the midpoint of each fit. The end values of the data are also evaluated from the first and the final fits.

In the general case of a least squares fit the function relationship between the two variables \( x, y \) may be written in the linear form:

\[
y = c_1 f_1(x) + c_2 f_2(x) + \ldots + c_m f_m(x)
\]

(5.40)

where \( c_n \) are the coefficients and \( f_n \) the functions. In the case considered here:

\[
\begin{align*}
f_1(x) &= x^2 ; \\
f_2(x) &= x \\
f_3(x) &= 1
\end{align*}
\]

(5.41)

with \( f_n = 0 \) for \( n > 3 \)

For a set of data points:

\[
S = \{(x_1, y_1); (x_2, y_2); \ldots (x_n, y_n)\}
\]

(5.42)

the least squares problem becomes one of minimizing the sum of the squares of the residuals \( \delta_i \) (\( i = 1, n \))

\[
\begin{align*}
c_1 f_1(x_1) + c_2 f_2(x_1) + \ldots c_m f_m(x_1) - y_1 &= \delta_1 \\
c_1 f_1(x_2) + c_2 f_2(x_2) + \ldots c_m f_m(x_2) - y_2 &= \delta_2 \\
& \vdots \\
c_1 f_1(x_n) + c_2 f_2(x_n) + \ldots c_m f_m(x_n) - y_n &= \delta_n
\end{align*}
\]

(5.43)
It can be shown, (Hamming 1962), that the values of \( c_i \) may be obtained from the solution of a set of linear equations:

\[
\sum_{i=1}^{n} a_{ki} c_i = b_k \quad \text{for } k = 1, 2, 3, \ldots, m \tag{5.44}
\]

where

\[
a_{ki} = \sum_{j=1}^{n} f_i(x_j) f_k(x_j)
\]

\[
b_k = \sum_{j=1}^{n} y_j f_k(x_j)
\]

(5.44) may be written in the matrix form:

\[
A \mathbf{c} = \mathbf{b}
\tag{5.45}
\]

\[
A = \mathbf{F}^T \mathbf{F}
\tag{5.46}
\]

\[
\mathbf{b} = \mathbf{F}^T \mathbf{y}
\tag{5.47}
\]

where \( \mathbf{F}^T \) is the transpose of \( \mathbf{F} \).

A number of methods are available for the solution of (5.45). The Gauss-Seidel iterative method was first tried but did not always converge and so was abandoned. The method of Gauss-elimination was then adopted since it always converged. The elimination procedure is discussed by Fox (1964) and in the case of (5.45) the method is particularly useful since matrix \( A \) is clearly symmetric (see equation after (5.44)). Since \( A \) is also positive definite, (i.e. \( \mathbf{x}^T A \mathbf{x} \) is positive for any real vector \( \mathbf{x} \)), the diagonals are non-zero and positive. The pivot points of the elimination were chosen down the diagonal thus ensuring a solution. The final solution of (5.45) was checked by determining the residual vector \( \mathbf{R} \):

\[
A \mathbf{C}_1 - \mathbf{b} = \mathbf{R}
\tag{5.48}
\]

where \( \mathbf{C}_1 \) is the Gauss-elimination solution. When, \( \left( \sum_{i=1}^{m} (x_i)^2 \right)^{\frac{3}{2}} < 10^{-4} \),
the fit was found to be accurate and no further action was taken. However if this condition was not fulfilled an iterative improvement method was applied. Writing:

\[ C_{n+1} = C + e \]  \hspace{1cm} (5.49)

where \( C \) is the real solution i.e. \( AC - b = 0 \) and \( e \) is the error vector that is required. From (5.48) we have:

\[ AC + A e - b = R \]  \hspace{1cm} (5.50)

hence

\[ A e = R \]  \hspace{1cm} (5.51)

Equation (5.51) is on the same form as (5.45).

Having solved the coefficient matrix the smoothed points can be generated from the midpoint of the set \( S \). This procedure is repeated for each consecutive set of 5 points.

The routine SMOOTH was designed to smooth up to 80 points using an odd value of \( n \) between 5 and 13. It was tested using the data of Spencer (1904) which is presented and discussed by Hildebrand (1956). A comparison was made by using a double 5 point least squares smooth and a 13 point smooth. These are shown with Spencer's data in Fig. 5.2.

The 5 point quadratic smoothing method was adopted in ADSEFF because of two reasons:

(i) The 5 point smoothing result indicates, as expected, that the curve follows more closely the data points but does smooth small irregularities.

(ii) The "end point" effect resulting from inadequate smoothing of the two extremes of the data set, are reduced using a 5 point smooth.

To record the amount of smoothing a relative smooth factor, \( (RSF) \), was defined:

\[ RSF = \left[ \frac{\sum_{i=1}^{n} \frac{|y(x_i) - y_i|}{y_i}}{n} \right] / n \]  \hspace{1cm} (5.53)
Fig. 5.2 Results of smoothing Spencer's (1904) data

Key:
- Spencer's data
- double 5 point quadratic smoothing result
- single 13 point quadratic smoothing result
where $y(x_i)$ is the smoothed point from (5.40) and $y_i$ the corresponding point. Typical values of RSF for experimental data were in the range $1 \times 10^{-2} - 5 \times 10^{-3}$.

### 5.4.3 Cubic Spline Interpolation

The data, $F(U)$ and $F(K)$, are handled in the program using cubic spline fits. This simplifies the determination of the numerical integrals and also allows the final distribution function to be obtained directly from the $F(U)$ splines. This method of interpolating is one of the most useful and advanced when dealing with data points at unequal intervals. It offers the advantage that the interpolation can be weighted at points where large changes in a function are expected. This is particularly needed when dealing with isotherm data that exhibits sharp discontinuities or "steps". In ADSEFF the spline fit is used to reproduce $F(K)$ and $F(U)$.

The fit is accomplished by connecting each pair of adjacent points with a section of a third degree polynomial, matching up the sections so that the first and second derivatives are continuous at each point. The equation of a cubic spline takes the form (Hamming 1962)

$$y = c_{1,j} (x_{j+1} - x)^3 + c_{2,j} (x - x_j)^3 + c_{3,j} (x_{j+1} - x) + c_{4,j} (x - x_j)$$

(5.54)

where the point $x$ lies between the data point $x_{j+1}$ and $x_j$. The constants $c_{1,j}$, $c_{2,j}$, $c_{3,j}$, and $c_{4,j}$ can be determined when the values of $y_j''$ are known.

$$c_{1,j} = y_j'' / 6 d_j$$
$$c_{2,j} = y_j''_{j+1} / 6 d_{j+1}$$
$$c_{3,j} = y_j / d_j - y_j''_{j} d_j / 6$$
$$c_{4,j} = y_j_{j+1} / d_{j+1} - y_j''_{j+1} d_{j+1} / 6$$

(5.55)
where \( d_j = x_{j+1} - x_j \).

Hamming (1962) has shown that the \( y_j'' \) values can be obtained by solving the matrix equation:

\[
A \mathbf{z} = \mathbf{b}
\]  

(5.56)

where

\[
A = \begin{bmatrix}
-\frac{1}{d_1} & \frac{1}{d_1} + \frac{1}{d_2} & -\frac{1}{d_2} & 0 & \cdots & 0 \\
p_1 & 2(p_1 + p_2) & p_2 & 0 & \cdots & 0 \\
0 & p_2 & 2(p_2 + p_3) & p_3 & \cdots & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots & \ddots \\
0 & \cdots & \cdots & \cdots & \cdots & p_{n-2} & 2(p_{n-2} + p_{n-1}) & p_{n-1} \\
0 & \cdots & \cdots & \cdots & \cdots & \cdots & -\frac{1}{d_{n-2}} & \frac{1}{d_{n-2}} + \frac{1}{d_{n-1}} & -\frac{1}{d_{n-1}}
\end{bmatrix}
\]

for a set of data points as (5.42)

where \( p_j = \frac{d_j}{6} \)

\[
\mathbf{b} = \begin{bmatrix}
0 \\
e_3 - e_2 \\
e_4 - e_3 \\
\vdots \\
0
\end{bmatrix}
\]

\[
\mathbf{e}_j = \frac{(y_j - y_{j-1})}{d_j}
\]

Because of the strong diagonal elements in \( A \) and its special nature, (5.56) can easily be solved.
The routine SPLINC that is used to determine \( c_1, c_2, c_3 \) and \( c_4 \) stores the values for subsequent use in the interpolation routine EVALUJT. This subroutine checks whether \( x \) is in the data range and if so proceeds to determine the nearest data points by starting at the centre of the array \( x \) and comparing magnitudes. Half steps are used to iterate to the position of the neighbours. The routines were checked, with generated data points from analytical functions, and found to be operational.

5.4.4 Trial Results

ADSEFF was tested by separately generating isotherms by using (5.1). To do this different Gaussian distribution functions were adopted. In the isotherm generation the Clenshaw-Curtis (1956) method of numerical integration was used, working to a relative accuracy of \( 10^{-6} \). The resulting data points were then input to ADSEFF and analysed using the same \( \Psi(P,U) \) function that was used in the isotherm generation.

The Gaussian function may be written in the form:

\[
\phi(U) = \frac{1}{n} \exp\left[-\gamma(U - U')^2\right]
\]

where \( n \) is the normalizing factor, \( U' \) the median of the distribution and \( \gamma \) the factor determining the range of the distribution. The larger the \( \gamma \) value the narrower the range and higher the maximum frequency. Table 5.4 lists the model isotherm and Gaussian functions that were used in testing ADSEFF. A narrow \( \gamma = 40 \) and a broader \( \gamma = 5 \) function were used together with a dual peak distribution function combining a \( \gamma = 5 \) and \( \gamma = 40 \) curve but normalized in the usual manner such that:
\[ n = \frac{U_h}{U_l} \int \exp\left[\gamma(U - U')^2\right] dU \]  

(5.58)

with \( U_l \) and \( U_h \) determined such that \( \psi(U_l) \) and \( \psi(U_h) = 0.001 \).

**TABLE 5.4** PARAMETERS USED IN \( \psi(U) \) FOR TESTING ADSEFF

<table>
<thead>
<tr>
<th>model isotherm function</th>
<th>( \gamma )</th>
<th>( U' ) /kcal.mol(^{-1})</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HdB</td>
<td>5</td>
<td>2.5</td>
<td>0.79267</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.5</td>
<td>0.28025</td>
</tr>
<tr>
<td></td>
<td>5, 40</td>
<td>2.5, 3.25</td>
<td>1.07028</td>
</tr>
<tr>
<td>Langmuir</td>
<td>5</td>
<td>4.0</td>
<td>ditto</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.5</td>
<td>ditto</td>
</tr>
<tr>
<td></td>
<td>5, 40</td>
<td>4.0, 4.75</td>
<td>ditto</td>
</tr>
<tr>
<td>FG</td>
<td>5</td>
<td>2.5</td>
<td>ditto</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.5</td>
<td>ditto</td>
</tr>
</tbody>
</table>

Figs 5.3 - 5.5 show the agreement between the generated distribution functions and the numerical points from ADSEFF. These are either produced from derivatives of the cubic spline fits to \( F(U) \) or by a direct gradient method i.e. from a straight line between data points on the \( F(U) \) function.

All the distributions shown in Table 5.4 gave similar results although the analysis using the Langmuir equation took more cycles to converge. For instance the FG and HdB functions took a maximum of 15 cycles but the Langmuir ran 20 cycles for the \( \gamma = 5 \), 50 for the \( \gamma = 40 \) and 90 for the dual peak distribution. All the results were the same whether SMOOTH was included or not.
The effect of decreasing the pressure range of the generated isotherm from $4.0 \times 10^{-6}$ torr to $1.0 \times 10^{-3}$ torr, is shown in fig. 5.6. Information about the higher energy sites is now absent and as expected the resulting distribution shows a higher frequency of the energy sites $> 2.4$ kcal mol$^{-1}$. This effect would be less obvious if the $U'$ value was lower.
Fig. 5.3 The results of the ADSEFF testing procedure using the Langmuir equation as the model isotherm function

Key:  
- - - \( \gamma = 5 \) Gaussian distribution function used in the isotherm generation program

- - - points obtained from the ADSEFF analysis of the generated isotherm
Fig. 5.4 The results of the ADSEFF testing procedure using the FG equation as the model isotherm function

Key: \( \gamma = 40 \) Gaussian distribution function used in the isotherm generation program

• • • points obtained from the ADSEFF analysis of the generated isotherm
Key:  \( \gamma = 5, \gamma = 40 \) dual peak Gaussian distribution

- - - points obtained from the ADSEFF analysis of the generated isotherm

Fig. 5.5 The results of the ADSEFF testing procedure using the HdB equation as the model isotherm function
Fig. 5.6 Results of the analysis by ADSEFF of the truncated isotherm generated using the HdB equation and a $\gamma = 5$ site energy distribution function.
APPENDIX 3

LISTING OF THE ALGORITHM FOR THE CALCULATION OF SITE ENERGY DISTRIBUTION FREQUENCY FUNCTIONS (ADSEFF)
ADSEFF  :  ALGORITHM FOR THE DETERMINATION OF SITE ENERGY
          FREQUENCY FUNCTIONS.

PROGRAM TO CALCULATE THE SITE ENERGY DISTRIBUTION FUNCTION BY
AN ITERATIVE PROCEDURE USING THE LANGMUIR, HILL-DE BOER OR THE
FOWLER-GUGGENHEIM MODEL ISOTHERM EQUATIONS.

WRITE (2,15)
15 FORMAT(///,40X,'--------------------------------------',//,
           120X,  ' ADSEFF : ALGORITHM FOR THE DETERMINATION OF SITE
           1 ENERGY FREQUENCY FUNCTIONS',///,20X,'==='.==='
           2   ==   ==  ',///,20X,' ORIGINATOR :
           3   WILLIAM A. HOUSF RSC, DIS, FCS, XVSO ',///,20X,'==='.==='
           4   NN=0

     DO 100 N=1,100
     READ (1,1) P(N),F(N)
1       FORMAT (2F0.0)
     IF(ABS(P(N)-9999.9) .LT. 1.0E-4)GOTO 2
     NN=NN+1
100    CONTINUE

F IS NOW THE VOLUME OF GAS ADSORBED IN CM**3(STP)/G
P IS THE EQUILIBRIUM BULK GAS PRESSURE MEASURED IN TORR.

     2 WRITE (2,3)
     3 FORMAT(///,51X,'INPUT DATA POINTS',///,51X,'------------------')
     CALL MONIT(NN,1)
     WRITE(2,4) NN

     4 FORMAT(///,40X,'NUMBER OF EXPERIMENTAL POINTS=',I3)
IF YESDS = TRUE THEN SUBROUTINE DATASET IS USED TO PROCESS INPUT
DATA: IF , FALSE THEN THE DATA IS USED IN THE FORM INPUT.

READ(1,36) YESDS
36 FORMAT (1A)
   IF(YESDS) CALL DATASET(NN)
   READ(1,37) YESSD
37 FORMAT (1A)
   READ(1,5) (GAS(J),J=1,2)
5 FORMAT (1A)
   WRITE (2,6) (GAS(J),J=1,2)
6 FORMAT (2X,'GAS;?2A8,1)
   READ(1,9) ICOUNT,ITFR,T,THLOW,THIGH,STEP,CON,GASCON
9 FORMAT (212,6F0.0)
   ISTART=ICOUNT
   VM=F(NN)

FIRST APPROXIMATION TO THE MONOLAYER VOLUME
READ(1,34) IFFFD
34 FORMAT (12)
   WRITE(2,11)
11 FORMAT (2X,'PRESSURE - VOLUME DATA NOW TO BE ANALYSED USING A
      NUMERICAL ITERATIVE METHOD',/,'20X','REFERENCES TO THE BASIS
      OF THE PROGRAM:',/,'25X','1. ADAMSON, A.W. AND LING, I., ADVAN.
      CHEM 1. SER., NO3, 51 (1961)',/,'25X','2. HOUSE, W.A. AND JAYCOCK, M. J., J.
      COLLOID AND INTERFACE SCI., 47, P50 (1974)',/,'40X','VALUES OF THE
      VARIABLES USED IN ANSEFF',/,'40X','-----------------------------
      1-----------------------------
5 FORMAT (1I)

IF VALUE OF MODEL=1 THEN THE HILL-DE ROER EQUATION IS USED
   IF MODEL=2 THEN THE FOWLER-GUGGENHEIM EQUATION IS USED.

   IF (MODEL ,EQ. 1) WRITE(2,10)
10 FORMAT (2X,'THE HILL-DE ROER EQUATION IS USED AS THE PATCH MODE
      ISOThERM FUNCTION',/)
   IF(MODEL, EQ. 2) WRITE(2,12)
12 FORMAT (2X,'THE FOWLER - GUGGENHEIM EQUATION IS USED AS THE MCD
      ISOThERM FUNCTION',/)

189
IF(MODEL .EQ. 3) WRITE(2,28)
28 FORMAT(/,27X,' THE LANGMUIR EQUATION IS USED AS THE PATCH MODEL
1 ISOTHERM FUNCTION,'/
WRITE(2,7) ISTART,ITF,T,VM,TLOW,THIGH,STEP,CON,GASCON
7 FORMAT(/,27X,' FIRST ITERATION NUMBER= ',I2,2X,' MAXIMUM NUMBER OF ITERATIONS ALLOWED= ',I2,2X,' ADSORBATE TEMPERATRUE IN DEGK= ',F8.4,12X,' MONOLAYER VOLUME INPUT TO ADSEFF= ',1,F8.4,2X,' LOWER COVERAGE VALUE AT STEP= ',E13.7,8X,' UPPER COVERAGE VALUE AT STEP= ',E13.7,2X,' PK VALUE OF THE STEP= ',E13.7,1X,' CONVERSION FACTOR IN(AO)= ',E13.7,' ',4X,' ADSORBATE SELF INTERACTION CONSTANT= ',F6.3,4X,' NOTE',/,' 4X,
1' ---',/,' 4X,' IF THE LANGMUIR FUNCTION IS USED OR THE ADSORBATE TEMPERATURE IS ABOVE THE TWO-DIMENSIONAL CRITICAL TEMPERATURE, THE 1' 4X,' STEP COVERAGE UNITS WILL BE EQUAL AND THE STEP PARAMETER WILL BE SET TO THE VALUE OF PK USED IN THE INITIAL APPROXIMATIONS. THIS STEP FUNCTION IS DEFINED THROUGH THE INFLECTION POINT OF THE MODEL PATCH ISOTHERM FUNCTION. IN ALL CASES',/,' 4X,' 1' PK=G(TETHA,T) WHERE G IS THE MODEL PATCH FUNCTION',/)
DO 200 J=1,NN
F(J)=F(J)/VM
K(J)=STEP/P(J)
C K(J) REFERS TO K IN THE STEP FUNCTION PK=STEP
C HENCE K=8 IN THE MODEL ISOTHERM FUNCTION PB=G(TETHA,T)
C AND NOT P=KG(TETHA,T) NORMALLY USED (IE K=1/B)
THEXP(J)=F(J)
200 U(J)=-0.001987*T*(ALOG(1.0/K(J)))-CON)
C ARRAYS F AND U NOW GIVE THE FIRST APPROXIMATION FOR THE DISTRIBUTION FUNCTION. ADSORPTION ENERGY, U, IN KCALS/MOL.
IF(ICOUNT .EQ. 1) GOTO 88
C IF ICOUNT NOT EQUAL TO 1 THEN DATA FOR F CORRESPONDING TO STARTING ICOUNT ITERATION IS REQUIRED.
READ(1,85) (F(J),J=1,NN)
85 FORMAT(4F0.4)
86 READ(1,41) YESPUNCH
41 FORMAT(16)
FLO=F(1)
FUP=F(NN)
KLO=K(NN)
KUP=K(1)
WRITE(2,13) FLOW,FUP
13 FORMAT(20X,'LOWER COVERAGE VALUE','E13.7,/,20X,'}
   'UPPER COVERAGE VALUE','E13.7)

C FUP AND FLOW ARE THE COVERAGE LIMITS OF THE EXPERIMENTAL
C ISOTHERM. FUP IS NORMALLY EXPECTED TO BE 1.0.

DO 250 J=1.50
   KDEL=NN-J+1
   A(J)=K(KDEL)
   A(KDEL)=K(J)
   B(J)=F(KDEL)
   R(KDEL)=F(J)
   C(J)=U(KDEL)
   C(KDEL)=U(J)
   KDFL=KDFL-J
   IF(KDFL.GT.2) GOTO 250
   IF(KDFL.EQ.2) GOTO 25
   IF(KDFL.EQ.1) GOTO 17
250 CONTINUE
25 A(J+1)=K(J+1)
   R(J+1)=F(J+1)
   C(J+1)=U(J+1)
17 WRITE(2,81) KLOW,KUP
81 FORMAT(20X,'LOWEST K='E13.7,/,20X,'HIGHEST K='E13.7)

DO 300 J=1,NN
   T1(J)=CALC(P(J)*KUP)
300 T2(J)=CALC(P(J)*KLOW)

14 CALL SPLINCA(A,R,NN,C1)
   SUMSO=0.0
   DO 400 J=1,NN
      CALL FQUAD(T2(J),T1(J),DETQ,RELACC,128,NPTS,ANS,0.0,PREANS)
      ADD=FUP*T2(J)+(1.0-T1(J))*FLOW
      PREANS=PRFANS+ADD
      THETA(J)=ANS+ADD
      PREAN(J)=PRFANS
      NP(J)=NPTS
      ADD=THEXP(J)-THETA(J)
      ADD=ADD/THFXP(J)
      SUMSQ=SUMSQ+ADD*ADD
      F(J)=F(J)*THFXP(J)/THETA(J)
IF(J .EQ. 1) GOTO 400
IF(F(J) .LT. F(J-1)) F(J)=F(J-1)+1.0E-6
400 CONTINUE
IF(ABS(F(NN)-1.0) .LT. 1.0E-4) GOTO 20
C ADJUSTS VM, THE XP AND F(J)'S IF UPPER LIMIT OF F NOT 1.0+/-1.0E-4
VM=VM*F(NN)
FNN=F(NN)
DO 410 J=1, NN
F(J)=F(J)/FNN
410 THFXP(J)=THFXP(J)/FNN
20 RMS2=RMS1
RMS1=SQR(T(SUMS0/FLOAT(NN))
RMS(ITCOUNT)=RMS1
IF(RMS1 .GT. RMS2) GOTO 31
C IF RMS INCREASES, THE PROGRAM GOES ON TO DETERMINE THE SITE
C ENERGY DISTRIBUTION FUNCTION FROM THE PREVIOUS U VS. F DATA
C OTHERWISE R IS RESET WITH THE NEW F VALUES AND THE ITERATIONS
C ARE CONTINUED.
IF(YFSSM0) CALL SMOOTH(K, F, 5, NN, RS1(ITCOUNT))
FUP=F(NN)
FLO=F(1)
DO 450 J=1, 50
KDEL=NN-J+1
R(J)=F(KDEL)
R(KDEL)=F(J)
KDEL=KDEL-1
IF(KDEL .GT. 2) GOTO 450
IF(KDEL .EQ. 2) GOTO 26
IF(KDEL .EQ. 1) GOTO 27
450 CONTINUE
26 B(J+1)=F(J+1)
27 IF(YFSSMO) CALL SMOOTH(C, R, 5, NN, RS2(ITCOUNT))
IF(ITCOUNT .EQ. ITER) GOTO 33
CALL FFD(CFFER, YESFEED, ICTOUNT)
IF(YFSFFFD) GOTO 33
ITCOUNT=ICTOUNT+1
GOTO 14
31 IF(YFSSMO) CALL SMOOTH(C, R, 5, NN, RS2(ITCOUNT))
33 CALL SUPERF(R, ISTART, ICTOUNT, NN)
WRITE(2, 32) VM
32 FORMAT(//,20X,'THE MONOLAYER VOLUME (SAME UNITS AS V INPUT)= ',E13.7)
   IF(RMS1 .GT. RMS2) ICOUNT=ITER
   USES THE SMOOTHED U Vs. F DATA TO GENERATE THE FIRST DERIVATIVE
   DEL F/ DEL U Vs. U TABLE.
   CALL SPLINCIC(C,R,NN,C1)
   WRITE(2,23)
23 FORMAT(//,30X,'U KCALS/MOL',10X,'FRACTION OF SURFACE PER UNIT
1 ENERGY INTERVAL //,30X,'----------------------------------',10X,'----------------------------------

USTFP=(U(1)-U(NN))/80.0
USUPST=USTFP/10.0
INTER=C(1)
ULOW=C(1)
UP=ULOW
DO 500 J=1,NN
   SUMSQ=0.0
   UUP=UP+USTFP
   DO 510 L=1,INTER
      CALL EVALUT(NN,C1,C,R,INTER,FINTER,2)
      SUMSQ=SUMSQ+FINTER
   510 INTER=INTER+USUPST
   FINTER=SUMSQ/INTER
   UINTER=(UUP+ULOW)/2.0
   IF(FINTER .GT. 0.0) FINTER=0.0
   WRITE(2,24) UINTER,FINTER
24 FORMAT(30X,F13.7,30X,E13.7)
   ULOW=ULOW+USTFP
500 ULOW=ULOW
30 ICOUNT=ICOUNT+1
   IF(ICOUNT .LE. ITER) GOTO 14
   NOW DETERMINE THE FINAL FREQUENCY CURVE BY DIRECT GRADIENT METHOD
   WRITE(2,39)
39 FORMAT(//,20X,'NOW CALCULATES THE FIRST DERIVATIVE BY THE DIRECT
1 GRADIENT METHOD: ',//,20X,'==============================================
1 '============================================== ',//,30X,'U KCALS/MOL',10X,
1 ' FRACTION OF SURFACE PER UNIT ENERGY INTERVAL ',//,30X,'----------------------------------

1 =- '10X,' ---------------------------------- ')
   DO 520 J=1,NN-1
   FINTER=(R(J)-R(J+1))/(C(J)-C(J+1))
```
UINTFR = (C(J+1) - C(J)) / 2.0 + C(J)
WRITE (2, 38) UINTFR, FINTER
38 FORMAT (30X, F13.7, 30X, F13.7)
520 CONTINUE
C
C FINAL F VALUE MAY BE OUTPUT IF YFSPUNCH=.TRUE.
C
IF (YFSPUNCH) WRITE (3, 40) (F(J), J=1, NN)
40 FORMAT (3 (F9.4, 1X))
STOP
END
```
SUBROUTINE DATASET(NN)
REAL K
LOGICAL YESML
DIMENSION C(4,A0),FF(80),PP(80)
COMMON K(80),F(80),P(80)
C
YOU REQUIRE MULTILAYER CORRECTION : TRUE OR FALSE
C
READ(1,?) YESML
2 FORMAT(16)
IF(YESML)CALL CORRECT(NN)
CALL SMOOTH(P,F,S,NN,RSF1)
CALL SMOOTH(P,F,S,NN,RSF2)
CALL SPLINC(P,F,NN,C)
PP(1)=P(1)
BASE=ALOG(P(1))
STRIP=(ALOG(P(NN))-ALOG(P(1)))/70.0
MM=0
DO 200 J=1,70
CALL EVALUT(NN,C,P,F,PP(J),FF(J),1)
BASE=BASE+STRIP
PP(J+1)=EXP(BASE)
IF(PP(J+1).GT.P(NN))GOTO 1
MM=MM+1
200 CONTINUE
1 NN=MM
DO 100 J=1,NN
F(J)=FF(J)
100 P(J)=PP(J)
WRITE(2,6) RSF1,RSF2
6 FORMAT(20X,1F13.7,/,20X,1F13.7)
WRITE(2,4)
4 FORMAT(/,40X,1F13.7,/,40X) CALL MONIT(NN,1)
WRITE(2,5) NN
5 FORMAT(/,40X,1F13.7,/) RETURN
SUBROUTINE CORRECT(NN)

REAL K
COMMON K(80), F(80), P(80)

IF USING THE MULTILAYER CORRECTION, INPUT PN, THE SATURATED VAPOUR PRESSURE OF THE ADSORBATE (UNITS: TORR)

READ(1,2) PN
2 FORMAT(F0.0)
WRITE(2,1) NN, PN
1 FORMAT (/,'20X,' MULTILAYER CORRECTION IS APPLIED TO THIS DATA OF ',1,12,' POINTS','20X,' THE SATURATED VAPOUR PRESSURE OF THE ADSORBATE IS ',F9.6)
MM=0
DO 100 J=1, NN
F(J)=F(J)*(1.0-P(J)/PN)
IF(F(J) .EQ. 1) GOTO 100
IF(F(J) .LT. F(J-1)) GOTO 3
100 MM=MM+1
GOTO 4
3 WRITE(2,5) NN, MM
5 FORMAT('20X,' DATA TRUNCATED ON USING MULTILAYER CORRECTION FROM ',1,12,' POINTS TO ',1,12,' POINTS')
NN=MM
4 RETURN
END
SUBROUTINE FEED(IFEED, YESFEED, ICOUNT)
LOGICAL YESFEED
IC=ICOUNT
IF(IFEED) 5,5,4
5 WRITE(2,6) IFEED
6 FORMAT(' ERROR IN SUBROUTINE FEED. THE VALUE OF IFEED INPUT= ', I14, ' IS OUT OF RANGE')
4 IF(IC - IFEED) 1,7,3
1 YESFEED = .FALSE.
RETURN
2 YESFEED = .TRUE.
RETURN
3 IC=IC-IFEED
GOTO 4
END
SUBROUTINE MONIT(NN,IP)

C ROUTINE TO MONIT PRESSURE - VOLUME OR ADSORPTION ENERGY - FRACTION
C OF SURFACE TO THE LINEPRINTER.
C
REAL K
COMMON K(80),F(80),P(80)/TWO/U(80)
JJ=1
IF ( IP .EQ. 2 ) GOTO 3
WRITE(2,1)
1 FORMAT(20X,4(' PRESSURE VOLUME',3X),/,
1       16X))
GOTO 4
3 WRITE(2,2)
2 FORMAT(21X,4(' U/KCALS FRACT ') )
4 KK=JJ+3
   IF ( KK .GT. NN ) KK=NN
   IF ( IP .EQ. 1 ) GOTO 7
   WRITE(2,5) ( U(J),F(J),J=JJ,KK)
5 FORMAT(20X,4(E10.4,1X,E10.4,1X))
GOTO 9
7 WRITE(2,8) ( P(J),F(J),J=JJ,KK)
8 FORMAT(20X,4(E10.4,1X,E10.4,1X))
9 IF ( KK .EQ. NN ) GOTO 6
   JJ=JJ+4
   GO TO 4
6 RETURN
END
FUNCTION CALCPK)

FUNCTION TO CALCULATE THETA FOR ANY MODEL GIVEN A PK INPUT VALUE.

COMMON /ONE/, MODEL, THLOW, THHIGH, STEP, I, GASCON, NN,
1A(80), R(80), C1(4,80), C2(4,80)
DATA ACC/1.0E-6/
IF (MODEL .EQ. 3) GOTO 8
IF (PK .GT. STEP) GOTO 1
IF (PK .LT. STEP) GOTO 2
CALC = THHIGH
RETURN
1 DELTH = (1.0 - THHIGH) / 2.0
THETA = THHIGH + DELTH
6 VAL = FUN(MODEL, THETA, GASCON) - PK
IF ((ABS(VAL / PK)) .LT. ACC) GOTO 4
IF (VAL .LT. 4) GOTO 5
5 DELTH = DELTH / 2.0
THETA = THETA - DELTH
GOTO 6
3 DELTH = DELTH / 2.0
THETA = THETA + DELTH
GOTO 6
2 IF (PK .LT. 0.01) GOTO 7
DELTH = (THLOW - 0.01) / 2.0
THETA = 0.01 + DELTH
GOTO 6
7 THETA = PK
DELTH = PK
GOTO 6
4 CALC = THETA
RETURN
8 CALC = PK / (1.0 + PK)
RETURN
END
FUNCTION FUN(MODEL, THETA, GASCON)

C FUNCTION TO OUTPUT PK GIVEN THE COVERAGE (THETA) INPUT.

C

IF (THETA .GE. 1.0) THETA = 0.99
IF (MODEL .EQ. 1) GO TO 1

C MODEL = 1 THEN FOWLER-GUGGENHEIM USED.
FUN = THETA/(1.0-THETA)*EXP(-GASCON*THETA)
RETURN
1 FUN = THETA/(1.0-THETA)*EXP(THETA/(1.0-THETA)-GASCON*THETA)
RETURN
END
FUNCTION DFTD(THETA)
REAL K, PK
COMMON K(80), F(80), P(80)/ONE/ MODEL, THLOW, THHIGH, STEP, J, GASCON, NN,
TA(80), T(80), C1(4, 80), C2(4, 80)
IF (THETA .GT. THLOW .AND. THETA .LT. THHIGH) GOTO 4
IF (MODEL .EQ. 1) GOTO 1
IF (MODEL .EQ. 2) GOTO 2
PK = THETA / (1.0 - THETA)
GOTO 3
1 PK = THETA / (1.0 - THETA) * EXP (THETA / (1.0 - THETA) - GASCON * THETA)
GOTO 3
2 PK = THETA / (1.0 - THETA) * EXP (-GASCON * THETA)
3 KI = PK / P(J)
GOTO 5
4 KI = STEP / P(J)
5 CALL EVALU(T(NN, C1, A, R, KI, FI, 1))
DFTD = FI
RETURN
END
SUBROUTINE SPLINE(X,Y,M,C)

ROUTINE TO DETERMINE THE SPLINE COEFFICIENTS FOR INPUT ARRAYS X,Y AND M POINTS. MATRIX C STORES THE SPLINE COEFFICIENTS.

DIMENSION D(80),E(80),F(80),A(80,3),R(80),Z(80),C(4,80),X(80),Y(80)

MM=M-1
DO 100 K=1,MM
D(K)=X(K+1)-X(K)
P(K)=D(K)/6.0
100 E(K)=(Y(K+1)-Y(K))/D(K)
DO 200 K=2,MM
200 R(K)=E(K)-E(K-1)
A(1,2)=-1.0+n(1)/D(2)
A(1,3)=n(1)/D(2)
A(2,3)=P(2)-P(1)*A(1,3)
A(2,2)=2.0*(P(1)+P(2))-P(1)*A(1,2)
A(2,3)=A(2,3)/A(2,2)
R(2)=R(2)/A(2,2)
DO 300 K=3,MM
A(K,2)=2.0*(P(K-1)+P(K))-P(K-1)*A(K-1,3)
R(K)=R(K)-P(K-1)*R(K-1)
A(K,3)=P(K)/A(K,2)
300 R(K)=R(K)/A(K,2)
Q=D(M-2)/D(M-1)
A(M,1)=1.0*n+A(M-2,3)
A(M,2)=Q-A(M,1)*A(M-1,3)
B(M)=R(M-2)-A(M,1)*R(M-1)
Z(M)=B(M)/A(M,2)
MN=M-2
DO 400 I=1,MM
K=M-1
400 Z(K)=R(K)-A(K,3)*Z(K+1)
Z(1)=A(1,2)*Z(2)-A(1,3)*Z(3)
DO 500 K=1,MM
Q=1.0/(6.0+n(K))
C(1,K)=Z(K)+Q
C(2,K)=Z(K+1)+Q

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\[ C(3, K) = v(K) / n(K) - z(K) * p(K) \]
\[ C(4, K) = v(K+1) / n(K) - z(K+1) * p(K) \]
RETURN
END
SUBROUTINE EVALUT(MIN,C,X,Y,XX,YY,MDIV)

ROUTINE TO EVALUATE YY AT INPUT XX FROM ARRAYS X,Y. THE NUMBER OF
POINTS IN THE ARRAYS IS MIN AND THE MATRIX CONTAINING THE
SPLINE COEFFICIENTS IS C.

I AND M ON COMPLETION OF THE PROCEDURE WILL CONTAIN THE TWO
NEAREST LOCATIONS IN X TO XX.

DIMENSION C(4,RO),X(RO),Y(RO)
DATA MSG/0/
M=MIN
ACC=XX*1.0E-4

TEST TO SEE IF XX IN THE RANGE OF X.

IF((X(1)-XX).GT.(1.0E-2)*X(1))GOTO 1
IF((XX-X(M)).GT.(1.0E-2)*X(M))GOTO 14
M=(M+1)/2
I=M
XXD=XX-X(M)
IF(ABS(XXD).LT.ACC)GOTO 3
IF(XXD).LT.ACC)GOTO 1
4 1=(I+1)/2
M=M+1
IF(M.GT.MIN)M=MIN
XXD=XX-X(M)
IF(ABS(XXD).LT.ACC)GOTO 3
IF(XXD).LT.ACC)GOTO 1
6 IF (1.LT.1) GO TO 7
GO TO 4
5 IF (1.LT.1) GO TO 8
2 1=(I+1)/2
M=M-1
IF(M.LT.0)M=1
XXD=XX-X(M)
IF(ABS(XXD).LT.ACC)GOTO 3
IF(XXD).LT.ACC)GOTO 1
3 YY=Y(M)
IF(MDIV .EQ. 2) GO TO 16
GO TO 13
7 S1=X(M)
S2=X(M+1)
I=M
GO TO 10
8 S1=X(M-1)
S2=Y(M)
I=M+1
GO TO 10
1 MSG=MSG+1
IF(MSG .GT. 10) GOTO 20
GO TO 13
14 MSG=MSG+1
IF(MSG .GT. 10) GOTO 20
GO TO 13
16 IF(M .EQ. 1) GOTO 17
S1=X(M-1)
S2=Y(M)
I=M+1
GOTC 19
17 S1=X(M)
S2=X(M+1)
I=M
GOTC 19
C MDIV=1 THEN FUNCTION INTERPOLATION
C MDIV=2 THEN FIRST DERIVATIVE INTERPOLATION.
C
10 IF(MDIV .EQ. 1) GO TO 13
19 YY=-3.0*C(2,1)*(S2-XX)**2+3.0*C(2,1)*(XX-S1)**2+C(3,1)+C(4,1)
GOTC 13
18 YY=C(1,1)*(S2-XX)**3+C(2,1)*(XX-S1)**3
+*C(3,1)*(S2-XX)+C(4,1)*(XX-S1)
13 RETURN
20 WRITE(2,11) XX,X(1),X(MIN),MIN,MDIV
11 FORMAT (/,'MESSAGE FROM EVALUT : PROGRAM TO FAIL DURING EXECUTION
11: BECAUSE INTERPOLATION VALUES OUTSIDE ARRAY RANGE',/,'20X,'1
11: THE TENTH TIME THIS HAPPENED THE FOLLOWING VALUES WERE IN STORE:
11: E13.7,'/,'20X,' THE INTERPOLATING VALUE OF XX= 'E13.7,'/,'20X,' THE LOW
1ST VALUE IN X = 'E13.7,/,20X', THE HIGHEST VALUE IN X = 'E13.7,/,20X',
THE DIMENSION OF X = 'E13,/,20X'. THE MDIV SWITCH IS SET TO
1 = 'I1,/,20X'. THIS FAILURE MAY BE CAUSED BY THE ACCURACY ATTAIN-
MENT IN CALC.'
STOP
END
SUBROUTINE QUAD(A,R,F,ACC,NMAX,N,ANS,ARSACC,PREANS)
EVALUATES A DEFINITE INTEGRAL BY THE CLENSCHAW-CURTIS METHOD.

DIMENSION X(63),XP(63),X4(63),FUN(63),WTS(132),NUM(6),COF(6)

IF (N) 1,R,8

THIS SECTION WHICH IS ONLY ENTERED IF N IS NEGATIVE CALCULATES
THE WEIGHTS AND PIVOTS.

1 C = 0.999698818698
S = 0.0245412282526
CN = C
SN = S

CALCULATE THE PIVOTS AND STORE THEM IN THE ARRAY X.

DO 2 I = 1,32
X(I) = CN
MM = 64-I
X(MM) = SN
T = SN*C+CN*S
CN = CN*C+SN*S
SN = T
X(32) = 0.7071067811865

CALCULATE THE WEIGHTS FROM ORDER 4 UP TO ORDER 128, AND STORE
THEM IN THE ARRAY WTS.

N = 4
N2 = 2
M = 32
L = 1
DO 5 NO = 1,6
NUM(NO) = L
ZN = N
C = X(M)
MM = 64-M
S = X(MM)
Z = 2.0/(2*N+2*N-1.0)
WTS(I) = 0.5*Z
\begin{verbatim}
L = I + 1
SJ = S
CJ = C
FN = 4.0/ZN
DO 4 J = 1,N
   C2J = 1.0-2.0*SJ*SJ
   S2J = 2.0*SJ*CJ
   SUM = 0.0
   DIV = 1.0
   SN = SJ
   CN = CJ
   DO 3 I = 1,N
      SUM = SUM+SN/DIV
   DIV = DIV+2.0
   T = SN*C2J+CN*S2J
   CN = CN*C2J-SN*S2J
3 SN = T
   Z = -2
   WTS(I) = Z+FN*SJ*SUM
   L = I + 1
   T = SJ*C+CJ*S
   CJ = CJ+C-SJ*S
4 SJ = T
   N2 = N
   N = N+N
5 M = M/2
   DO 6 I = 1,N/2
      C = X(I)
      C = 2.0*C*C-1.0
      X2(I) = C
6 X4(I) = 2.0*C*C-1.0
C SET UP COEFFICIENTS COF(I) FOR THE CLENSHAW-CURTIS
C ERROR ESTIMATES.
C
COF(1) = 6.09523809522E+1
COF(2) = 7.3881673813E+2
COF(3) = 4.6445979200F+3
COF(4) = 4.93092372956E+4
COF(5) = 6.1764999641F+5
\end{verbatim}
$\text{COF}(a) = 7.63405373194 \times 10^{-6}$

*THE CLENSHAW-CURTIS INTEGRATION BEGINS AT THIS POINT.*

```
8 IF (A-B) < 8.39E-3
38 ERR = ACC
   IERROR = 0
   END = F(A)+F(B)
```
HPND = 0.5*FND
HAF = 0.5*(R-A)
HAF4 = 0.25+HAF
AMID = 0.5*(R+A)
CENT = F(AMID)
HCNP=HPND+CENT
HCNP = HPND-CENT
ZA = HAF*0.7071067811865
ZB = AMID-ZA
ZA = AMID+ZA
FUN(1) = F(ZA)+F(ZB)
NORDFR = 7
PREANS = HAF*(WTS(1)*FEND+WTS(2)*FUN(1)+WTS(3)*CENT)

PREANS IS THE ESTIMATE OF THE INTEGRAL FOR N = 4.

PREST = 0.3047619047619*HAF*ABS(HEND-FUN(1)+CENT)
IF (PREANS) < 0.5, 50
50 PREST = PREST/PREANS

CALCULATE THE INTEGRAL, BEGINNING WITH N = 8.

51 N = 8
13 N4 = N/4
N2 = N4+N4
ZN = N
ZN2 = N2
LC = N4-1
LA = LC+LC
LR = LC
DO 14 J = 1, LR
FUN(LA) = FUN(LC)
LA = LA+2
14 LC = LC+1
LA = 1
LB = 128/N
DO 15 J = 1, N4
MM = LA+LR
P = X(MM)*HAF
ZA = AMID-P
ZR = AMID+P
FUN(1A) = F(7A)+F(ZR)

LA = LA+2
M = NUM(NORDER)
MM = M*N2
ANS = WTS(N)*FND+WTS(MM)*CENT
AN = HCP
AN2 = HCM
AN4 = AN
W = -1.0
N21 = N2-1
DO 16 J = 1,N21
JL = J*LR
WF = W*FUN(J)
AN = AN+WF
AN2 = AN2+WF*X2(JL)
AN4 = AN4+WF*X4(JL)
W = -W
MM = M+J
16 ANS = ANS+WTS(MM)*FUN(J)
AN = HAF*ABS(AN)/ZN2
AN2 = HAF*ABS(AN2)/ZN
AN4 = HAF4*ABS(AN4)/ZN
ANS = HAF*ANS

C
C ANS IS THE ESTIMATE OF THE INTEGRAL FOR ORDER N.
C

AMAX = AN
IF (AN2-AMAX) 18,18,17
17 AMAX = N2
18 IF (AN4-AMAX) 20,20,19
19 AMAX = AN4
20 IF (ANS) 52,53,52
52 EST = ARS(COF(NORDER)*AMAX/ANS)
ACAL = ARS(EST*ANS)
GO TO 21
53 EST = ARS(COF(NORDER)*AMAX)

C
C EST IS THE RELATIVE ESTIMATE OF THE ERROR, OR THE ABSOLUTE
C ESTIMATE IF ANS IS ZERO.
C
21 IF (FST-ERR) 22,22,26
22 IF (IERRO) 23,23,31
23 IF (AN-AN2) 24,24,25
24 IF (PREANS) 41,40,41
40 IF (ANS) 27,31,27
41 IF (ABS(1.0-ANS/PREANS)-PREST) 31,31,25
C
25 IF (N=64) 32,33,33
32 ERR = 0.1*FRR
    GO TO 34
33 ERR = 0.01*FRR
34 IERROR = 1
    GO TO 21
26 IF (N-NMAX) 27,28,28
C
27 IF (ARCAL .LT. ARSACC) GO TO 28
    N=N+N
    NORDER = NORDER+1
    PREANS = ANS
    PREST = EST
    GO TO 13
C
28 N=N+1
    RETURN
C
31 N=N+1
    RETURN
C
39 ANS = 0.0
    N = 0
    RETURN
END
SUBROUTINE SMOOTH(C,R,NPT,NN,RSF)

ROUTINE TO SMOOTH INPUT DATA IN ARRAYS C AND R. THE ARRAY C IS NOT ALTERED BUT R IS SMOOTHED BY A NPT POINT (MAXIMUM 13) SUCCESSIVE QUADRATIC FITTING PROCEDURE. EVALUATION OF THE SMOOTHED FUNCTION IS AT THE MIDPOINT OF THE QUADRATIC FIT.

INTEGER CLOW,CUP
DIMENSION B(R0),C(R0),X(13),Y(13),CQ(3)
RSF=0.0

RSF IS THE RELATIVE SMOOTHING FACTOR OUTPUT FOR EACH RUN OF SMOOTH

NP=NPT
DO 100 J=1,NP
   X(J)=C(J)
   Y(J)=R(J)
   CALL COFF(Y,Y,CQ,NP)
   K=(1+NP)/2
   DO 200 J=1,K
      F=CQ(1)+CQ(2)+CQ(3)+CQ(J)*C(J)
      RSF=RSF+ABS((F-R(J))/R(J))
   200 B(J)=F
   CLOW=K
   CUP=NP+1
   DO 300 J=1,K
      X(J)=C(J-1+CLOW)
      Y(J)=R(J-1+CLOW)
      CALL COFF(Y,Y,CQ,NP)
      J=(CLOW+CUP)/2
      F=CQ(1)+CQ(2)+CQ(3)+CQ(J)*C(J)
      RSF=RSF+ABS((F-R(J))/R(J))
      B(J)=F
   300 IF(CUP.EQ.NN)GOTO 2
      CLOW=CLOW+1
      CUP=CUP+1
      GOTO 2
   1 F=CQ(1)+CQ(2)+CQ(3)+CQ(NN)+CQ(3)*C(NN)*C(NN)
   2 F=CQ(1)+CQ(2)+CQ(3)+CQ(M)+CQ(3)*C(M)*C(M)

213
RSF = RSF + ARS ((F-R(M))/B(M))
400 B(M) = F
   RSF = RSF / FLOAT(NN)
   RETURN
   END
SUBROUTINE COEF(X,Y,C,NN)

UP TO 13 VALUES X, Y MAY BE INPUT TO DETERMINE THE LEAST SQUARES QUADRATIC COEFFICIENTS Y=C(1)+C(2)*X+C(3)*X**2

*DIMENSION X(13),Y(13),A(3,3),B(3),C(3)*
B(1)=0.0
B(2)=0.0
B(3)=0.0
A(1,1)=NN
A(1,2)=0.0
A(1,3)=0.0
A(2,1)=0.0
A(2,3)=0.0
A(3,1)=0.0
A(3,2)=0.0
A(3,3)=0.0
DO 100 1=1,NN
B(1)=B(1)+Y(I)
R(2)=B(2)+Y(I)*X(I)
R(3)=R(2)+Y(I)*X(I)*X(I)
A(1,2)=A(1,2)+Y(I)
A(1,3)=A(1,3)+Y(I)*X(I)
A(2,2)=A(2,2)+Y(I)*X(I)^2
A(3,2)=A(3,2)+Y(I)*X(I)^3
A(3,3)=A(3,3)+Y(I)*X(I)^4
100 CONTINUE
A(2,1)=A(1,2)
A(3,1)=A(1,3)
A(2,2)=A(1,3)
A(3,2)=A(2,3)
CALL GAUSSIAN(A,B,C)
RETURN
END
SUBROUTINE GAUSSSLIM(AA, BB, C)
REAL M
DIMENSION A(3, 3), AA(3, 3), B(3), C(3), R(3), RR(3), P(3)
C SOLVES LEAST SQUARES MATRIX FOR QUADRATIC COEFF. BY THE METHOD
C OF GAUSS ELIMINATION FOR A SYMMETRICAL MATRIX.
C REFINEMENT IS OBTAINED USING THE RESIDUAL MATRIX METHOD.
ICOUNT=1
DO 300 J=1, 3
300 R(J)=BB(J)
1 DO 100 J=1, 3
DO 200 JJ=1, 3
200 A(J, JJ)=AA(J, JJ)
100 CONTINUE
M(1)=-A(2, 1)/A(1, 1)
M(2)=-A(3, 1)/A(1, 1)
A(2, 2)=A(2, 2)+M(1)*A(1, 2)
A(2, 3)=A(2, 3)+M(1)*A(1, 3)
A(3, 2)=A(3, 2)+M(2)*A(1, 2)
A(3, 3)=A(3, 3)+M(2)*A(1, 3)
B(2)=B(2)+M(1)*B(1)
B(3)=B(3)+M(2)*B(1)
M(3)=-A(3, 2)/A(2, 2)
A(3, 3)=A(3, 3)+M(3)*A(2, 3)
R(3)=B(3)+M(3)*R(2)
C(3)=B(3)/A(3, 3)
C(2)=(B(2)-A(2, 3)*C(3))/A(2, 2)
C(1)=(B(1)-A(1, 3)*C(3)-A(1, 2)*C(2))/A(1, 1)
IF (ICOUNT .EQ. 0) GOTO 10
C(1)=P(1)-C(1)
C(2)=P(2)-C(2)
C(3)=P(3)-C(3)
10 R(1)=0.0
R(2)=0.0
R(3)=0.0
DO 450 K=1, 3
DO 500 J=1, 3
500 R(K)=R(K)+AA(K, J)*C(J)
450 CONTINUE
ERR=0.0
DO 550 J=1, 3
\( R(J) = R(J) - R(J) \)

550 \( ERR = FRR + A(J) * R(J) \)
\( ERR = \text{SORT}(FRR) \)
\( I\text{COUNT} = I\text{COUNT} + 1 \)
\( \text{IF}(ERR \lt 1.0 \leq 2) \text{GOTO} 4 \)
\( \text{IF}(I\text{COUNT} \leq 3) \text{GOTO} 4 \)
\( \text{DO} 650 \quad J = 1, 3 \)

650 \( P(J) = C(J) \)
\( \text{GOFC} 1 \)
4 \( \text{RETURN} \)

END
SUBROUTINE SURROUNDS(P,ISTART,ICOUNT,NN)

ROUTINE TO OUTPUT RESULTS IF MAXIMUM ITERATIONS REACHED OR RMS
HAS REACHED A MINIMUM.

DIMENSION P(80)
COMMON/FOUR/ THETA(80), THEXP(80), RMS(100), NP(80), PREAN(80), RS1(100
1), RS2(100)
WRITE(2,5) ICOUNT
5 FORMAT(//,4RX, ' RESULTS AFTER ', I3, ' CYCLES', //, 4RX, ' WEIGHT 

WRITE(2,5) I
1 FORMAT(17X, ' ITERATION NUMBER:  ROOT MEAN SQUARE ', 
1 ' RELATIVE SMOOTHING  RELATIVE SMOOTHING', //, 39X, ' DEVIATION', 
110X, ' FACTOR(K,F)', 9X, ' FACTOR(U,F)'
WRITE(2,2) ((J, RMS(J), RS1(J), RS2(J)), J=ISTART, ICOUNT)
2 FORMAT(24X, I3, 10X, E13.7, 7X, E13.7, 8X, E13.7)
WRITE(2,2) 
3 FORMAT(/,3X, ' PT.NO. PRESSURE/TORR THETA(CALC.) THF 
1TA(EXP) THETA DIFF DIFF. PREV.INTEGRAL',//)
DO 100 J=1,NN
ADD=THEXP(J)-THETA(J)
WRITE(2,4) J, P(J), THETA(J), THEXP(J), ADD, NP(J), PREAN(J)
CONTINUE
WRITE(2,6)
6 FORMAT(//,20X, ' -----------------------------------------------' 
1-----------------------------------------------',//)
CALL MONIT(NN,?)
RETURN
END
CHAPTER 6

EXPERIMENTAL METHOD

6.1 VACUUM SYSTEM

All of the experimental adsorption isotherms were measured using the high vacuum frame that is shown in figs 6.1 and 6.2. The pumping system consisted of a double chamber Edwards model ED 100 rotary pump, with a displacement volume of 100 litres min⁻¹ and capable of an ultimate vacuum of $2 \times 10^{-4}$ torr, and a three stage mercury diffusion pump in which the mercury boiler pressure was maintained at about 10 torr. A liquid nitrogen trap was incorporated between the pumps and the main working volume.

The vacuum frame was constructed of borosilicate glass. The main connecting tubes were made of 2 mm. internal diameter, thick walled tubing. The taps were conventional vacuum taps used with Apiezon N grease. The sample under investigation was connected to the frame using a B7/16 joint and Apiezon T grease which enabled the sample to be heated during the sample degassing periods or when the sample was annealed at high temperatures. The internal volume of the vacuum system was varied by successive filling of calibrated burettes with tri-distilled mercury. The sizes of these burettes were determined by Waldsax (1970) to facilitate adsorption measurements with samples of between 1 - 10 m² in surface area, although it could be used for areas of slightly less than this if krypton gas was used. As shown in fig. 6.1, the entire working volume was enclosed within a thermostated cabinet. Two blackened 60 watt bulbs and two fans were used to maintain an even distribution of temperature to within ±0.1°C. The "light guide effect" (Sidebottom 1967) observed by
Fig. 6.1 Adsorption measurement apparatus
Fig. 6.2 Adsorption measurement apparatus showing Baratron gauges, McLeod gauge and burettes inside the thermostated cabinet.
Rosenberg and Martel (1957) was eliminated for the tube leading to the sample by painting the outside surface black above the liquid nitrogen level and covering the tube inside the liquid nitrogen bath with blackened copper foil.

The frame included a saturation vapour pressure manometer. This was filled with nitrogen gas to a pressure of 800 torr and during use the pressure readings were taken directly from a metre scale.

The pressure measurements made in the investigation of the thermal transpiration of krypton described in §6.2 were made using McLeod gauges. These gauges were later replaced by capacitance manometers as shown in fig. 6.1. One McLeod gauge was retained as shown in fig. 6.1 and was used for checking the vacuum during the zero adjustment of the capacitance manometers.

The McLeod gauge was based on a design by Jaycock and Sidebottom and has previously been described by Sidebottom (1967). The main modifications from the conventional design were:

(i) an addition of a third limb connected to the main vacuum line to give a direct measurement of the pressure in the closed limb of the McLeod gauge.

(ii) a 2mm internal diameter orifice to the McLeod compression volume similar to that used by Podgurski and Davis (1960). This allowed a rapid "cut off" and isolation of the compression volume and minimized errors in the system volume due to the setting of the mercury level.

It was also observed that the capillary depression of the mercury meniscus in the 2mm standard bore capillary, used in the construction of the closed limb and the reference limb of the McLeod gauge, did not cancel. After dismantling the gauge and cleaning with 60/40 nitric acid, chromic acid and washing with tri-distilled water and
distilled acetone, it was found that after refilling with fresh tri-
distilled mercury the same error remained. To overcome this diffi-
culty, a substantial one if the required accuracy at low pressures
in the thermal transpiration work was to be attained, the third
reference limb was replaced by a 16mm tube in which the capillary
depression was negligible. The closed limb capillary depression was
then measured over its entire length. With the results of over fifty
readings, a scatter diagram of the capillary depression was plotted
and used in all subsequent measurements of pressure. The capillary
depression was periodically checked and when necessary recalibrated.
In this manner it was possible to reduce the maximum error at low
pressures, i.e. in the region of $8 \times 10^{-3}$ torr, to 1.5%. The capil-
lary depression variations for the 2mm. capillary were of the same
order as those reported by Jansen and Venema (1959) for a similar
diameter capillary. The lowest pressure that could be measured was
$2 \times 10^{-3}$ torr. Below this pressure problems arise because the
vapour pressure of mercury at 25°C is $1.68 \times 10^{-3}$ torr. In an attempt
to reduce the effects of mercury, gold foil was introduced into the
upper regions of the sample tube above the liquid nitrogen level with
each new sample. However mercury vapour still rapidly condensed at
the cold junction on immersion of the sample tube into liquid nitrogen.

All the isotherms were measured using capacitance manometers,
M.K.S. Baratrons type 145AH-1 and 145AH-10 capable of measuring
pressures as low as $10^{-5}$ torr. The Baratron head, 145AH-1, covered
the pressure range of $10^{-5}$ - 1 torr with a quoted error maximum of
10% at $10^{-5}$ torr to 0.08% at 1 torr on a linear scale. The head,
145AH-10, covered the range $10^{-4}$ torr - 10 torr with a similar error
range to the other head. Integral heaters were provided in each of
the heads so that they could be thermostated at a temperature of
49 ± 0.14°C during normal use, and to allow rapid outgassing by baking at 71°C. The heads may be used unheated but the readings are subject to fluctuation. The problem of the thermal transpiration effect associated with heated heads is discussed in §6.4.2. The electronic unit type 170M - 5A was used to provide power to the heads and convert the head output to a proportional DC output of ±10V DC full scale. The voltage was directly output from the control unit to a Solatron 5 figure DC digital voltmeter (model: LM1604).

In the present work the heads were used in the differential measurement configuration with reference port connected via a Cajon coupling and a Kovar-pyrex seal to the main vacuum line. A nitrogen storage bulb was incorporated in the reference line in order to provide a backing pressure for pressure measurements greater than 10 torr. The heads were placed at such a height to prevent accidental mercury spoilage and so that they could be easily isolated from the rest of the system.

6.2 THE THERMAL TRANSPARATION EFFECT FOR KRYPTON

6.2.1 Introduction

At low adsorption pressures the sharp thermal junction at the liquid nitrogen-air interface can cause a pressure differential inside the sample tube.

At very low pressures when the number of collisions in the gas state are very much smaller than collisions with the wall, equilibrium is established when the number of molecules which cross unit cross-section normal to the temperature gradient in 1 second in either direction is the same. This condition gives rise to the Knudsen equation, $P_1 = P_2 \sqrt{\frac{T_2}{T_1}}$, where $P_1$ is the pressure in torr at the lower temperature, $T_1$, and $P_2$ is the pressure in torr at the higher
temperature, $T_2$.

At intermediate pressures two opposing gas flows become important:

(i) an axial flow from the hotter to the colder region. This is the normal flow in a very wide tube which results in pressure equilibration of the system.

(ii) a surface flow along the walls in the reverse direction to that flow described in (i). The atoms striking a rough surface are repelled in a direction independent of their angle of incidence. Consequently more atoms will be deflected into the warmer region per unit time than will be deflected in the opposite direction.

At equilibrium these two effects must be equal. Liang (1955) divides the atom collisions into the bulk phase collisions and the wall collisions and determines a pressure contribution from both. In this manner Liang (1955) was able to propose a semi-empirical equation of the form:

$$ R = \frac{P_1}{P_2} = \frac{a_{He}(\phi X)^2 + \beta_{He}(\phi X) + R_m}{a_{He}(\phi X)^2 + \beta_{He}(\phi gX) + 1} \quad (6.1) $$

where:

- $R_m = \text{Knudsen's constant} = \left(\frac{T_1}{T_2}\right)^{\frac{3}{2}}$
- $X = P_2 d$
- $d = \text{internal diameter, in mm., of the tube at the junction}$
- $a_{He}$ and $\beta_{He}$ are experimental constants
- $\phi$ is a factor specific to the gas under consideration and defined equal to 1 for helium. Values for the experimental constants in Liang's equation have been proposed by Bennett and Tompkins (1957), but these were in poor agreement with the experimental data of Rosenberg (1956) and Rosenberg and Martel (1958). Previously Sidebottom (1967), Waldsax (1970), House and Jaycock (1974a) have
used Laing's equation, with constants from Rosenberg (1956), for krypton gas only in the region of $X > 0.075$ torr mm. For the region of $X < 0.075$ torr mm., the equation developed by Weber (1937) and Miller (1963) fits the Rosenberg's observed values quite well when a value for the hard sphere diameter of krypton of $4.20\AA$ is used.

The Weber-Miller equation takes the form:

$$ R = 1 - (1 - R_m)/(\alpha y^2 + \beta y + \mu) $$

(6.2)

where

$$ y = X\sigma^2/kT $$

$$ \sigma = \text{molecular hard-sphere diameter} $$

$$ T = (T_1 + T_2)/2 $$

$$ \mu = (1 + 2.5y)/(1 + 2y) $$

and $\alpha$ and $\beta$ are constants having the values of $\alpha = 0.03$ and $\beta = 0.262$ for krypton.

More recently Takaishi and Sensui (1963) have proposed an equation somewhat similar to Liang's:

$$ R = 1 + \frac{R_m - 1}{A^*(X/T)^2 + B^*(X/T) + C^*(X/T)^{0.5} + 1} $$

(6.3)

where $R_m$ and $T$ have the same significance as before, and $A^*$, $B^*$ and $C^*$ are experimental constants having the values of $14.5 \times 10^5$/deg.$^2$ mmHg$^{-2}$ mm.$^{-2}$, $15.0 \times 10^2$/deg. mmHg$^{-1}$ mm.$^{-1}$ and $13.7$/deg.$^{1/2}$ mmHg$^{-1/2}$ mm.$^{-1}$ respectively for krypton.

Mason, Evans and Watson (1963), have proposed a theory they call the "Dusty Gas Theory" which has a general form bearing relationship to both Weber and Liang's equation. In its full form it contains five parameters which are difficult to determine experimentally, however it reduces, if certain approximations are made, to either (6.1) or (6.2). The theory predicts the following values for the
constants of the Liang equation: $\alpha_{\text{He}} = 2.52/\text{mmHg}^{-2} \text{mm}^{-2}$, $\beta_{\text{He}} = 4.46 \text{ mmHg}^{-1} \text{ mm}^{-1}$ and $\phi_g = 1.99$ (obtained using the hard sphere diameters from Hirschfelder, Curtiss and Bird 1954). The $\beta_{\text{He}}$ and $\phi_g$ values are in poor agreement with the experimental values determined in this work (see Table 6.1).

Computation of $R$ as a function of $X$, fig. 6.3, shows considerable discrepancy between the predictions of the equation of Liang, Weber, and Takaishi and Sensui, particularly in the low pressure region. Since accurate determination of physical adsorption isotherms for krypton at low pressure necessitates accurate thermal transpiration correction, work was undertaken to establish the best form of the correction.

6.2.2 Experimental

The two experimental methods adopted were the relative method as used by Los and Ferguson (1952) and the comparative method of Rosenberg and Martel (1958). In the former method the pressure difference across the upper ends of a Pyrex U-tube with dissimilar limbs was measured. The tube consisted of a wide limb, $18.955 \pm 0.003\text{mm. internal diameter}$ and a narrow limb of either $0.999 \pm 0.003$, or $2.018 \pm 0.003$, or $13.964 \pm 0.002\text{mm. diameter}$. These measurements were obtained using the mercury 'slug' method.

The U-tube was immersed to a constant level in a liquid nitrogen bath, the temperature of which was controlled at 77.7K by the addition of small quantities of liquid air or nitrogen. The bath was stirred continuously and the temperature measured by means of the nitrogen vapour pressure thermometer using the data of Friedman and White (1950). The upper temperature was room temperature equal to $293.3 \pm 1.0\text{K}$. This mean temperature was used in all calculations from
Fig. 6.3

Key:

- ○ Experimental data using the relative method
- Liang function fitted in this work
- □ Rosenberg's (1956) points
- --- Weber-Miller function fitted by Sidebottom (1967)
- --- --- Function of Takaishi and Sensui (1963)
Fig. 6.4  Thermal transpiration results

Key: ○ high pressure data obtained using the relative method
      — Liang function with constants evaluated in this work
Fig. 6.5 Thermal transpiration results

Key:
- ○ low pressure data determined using Rosenberg's (1956) comparative method
- Liang function with constants evaluated in this work
theoretical equations, but room temperatures were used in calculating experimental data. Corrections for thermal transpiration in the wide limb were made where necessary.

In the Rosenberg method a tube of total length 25 cm. was constructed from three 7 cm. lengths of the 19, 2 and 1 mm. diameter tubes with a sample bulb at the bottom containing carbon black with a total surface area of 10 m$^2$. The quantity of carbon black was chosen so that altering the position of the cold junction produced negligible change in the pressure above the adsorption sample. The two McLeod gauges employed were of the design that was discussed in § 6.1.

6.2.3 Results and Analysis

The experimental results that were obtained using the relative method are shown in figs 6.3 and 6.4. Those results obtained using the comparative method are shown in fig. 6.5. The data of Rosenberg and Martel (1958), obtained using the relative method, are also shown in fig. 6.3 together with the Weber-Miller function.

The predicted values of $R$ using equation (6.3) and the constants of Takaishi and Sensui are also plotted in fig. 6.3. Takaishi and Sensui's function shows poor agreement with any other data.

The present results were analysed using the Liang equation for the entire X range. Bennett and Tompkins (1957) have independently determined the parameters for (6.1). By writing $\Delta P = P_2 - P_1$, substituting in (6.1) and rearranging to give $\Delta P$ as a function of $P_2$, an equation is obtained which exhibits a maximum, the position of which is given by:

$$a_{He}(\phi X)^2_{\text{max}} = 1$$

(6.4)

Liang assumed $a_{He}$ and $\phi$ to be independent of temperature, thus the
position of the maximum should be independent of temperature. Bennett and Tompkins showed that this was not the case and that either $a_{\text{He}}$ or $g$ or both were temperature dependent. For convenience $g$ was assumed to be temperature independent and the following expression was presented for $a_{\text{He}}$:

$$a_{\text{He}} = 208.2(1.7 - 2.6 \times 10^{-3}(T_2 - T_1))^{-2} \quad (6.5)$$

By means of fig. 6.6 and equations (6.4) and (6.5), $g$ was evaluated. The position of the maximum lies within the range of $P_2 = 0.15$ to 0.17 torr. A mean value gives $g = 3.70$. The low pressure data obtained by the relative method are shown in fig. 6.3 together with the Liang equation plotted with the constants determined above. These results are confirmed by the analysis using the comparative method (fig. 6.5). The Liang equation also provides a good fit to the experimental data in the high pressure region (fig. 6.4). The various constants for the Liang equation are summarized in Table 6.1.

**TABLE 6.1 CONSTANTS USED IN THE LIANG EQUATION**

<table>
<thead>
<tr>
<th>$a_{\text{He}}$/mmHg$^{-2}$</th>
<th>$a_{\text{He}}$/mm$^{-2}$</th>
<th>$\beta_{\text{He}}$/mmHg$^{-1}$/mm$^{-1}$</th>
<th>$\beta_{\text{He}}$/mm$^{-1}$/mm$^{-1}$</th>
<th>$\phi$</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.52</td>
<td>141.8</td>
<td>7.68$(1-R_m)$</td>
<td>57.6$(1-R_m)$</td>
<td>3.84</td>
<td>Rosenberg (1956)</td>
</tr>
<tr>
<td>2.85</td>
<td>160.3</td>
<td>7.88$(1-R_m)$</td>
<td>59.1$(1-R_m)$</td>
<td>3.9</td>
<td>Bennett and Tompkins (1957)</td>
</tr>
<tr>
<td>2.85</td>
<td>160.3</td>
<td>7.88$(1-R_m)$</td>
<td>59.1$(1-R_m)$</td>
<td>3.7</td>
<td>This work</td>
</tr>
</tbody>
</table>
Fig. 6.6 The determination of $X_{\text{max}}$

$d = 0.999$ mm
The fact that the Liang equation predicts the thermal transpiration behaviour of krypton is consistent with the conclusions of Podgurski and Davis (1961), that this equation is satisfactory for both argon and xenon.

Two further points were considered, both of interest to the study of physical adsorption of gases. Firstly the effect of varying the capillary wall thickness was investigated and no experimental differences in the value of R were observed between a 0.999 mm diameter capillary of 3.48 mm wall thickness, and a 1.505 mm diameter capillary with a 1.012 mm wall thickness. Secondly the use of a glass filler rod in a sample tube to reduce 'dead volume' was investigated using a 1 mm diameter rod in a 2 mm capillary. The correction factor was higher: For example with $P_2 d = 0.324$ mmHg mm, the value of R is increased from 0.950 to 0.962. Thus it may well be possible with a larger tube and filler rod to investigate the BET range ($0.13 < P_2 < 0.89$ mmHg) without the necessity of using thermal transpiration corrections, although the specific case needs further study.

6.3 THE PREPARATION OF SODIUM CHLORIDE

6.3.1 Introduction

A number of methods of preparation of cubic crystalline sodium chloride have been used by previous workers. Many of these, particularly Craig and McIntosh (1952), Moffat and McIntosh (1957) have been solely concerned with the preparation of samples with large specific surface areas and the role of sintering during their preparations. Benson and Benson (1955) have also been concerned with the preparation of high area samples for surface enthalpy measurements. However, much of the work concerning the physical adsorption of gases onto sodium chloride has been hindered because of the difficulties in
preparing high area samples. In spite of this difficulty, Orr (1939),
developed a method of measuring gas adsorption on alkali halide
crystals of low specific surface area, and later Hayakawa (1957a)
adsorbed argon on cubic sodium chloride that was prepared by re-
crystallization from solution. The sample used by Hayakawa had a
specific area of \( \approx 0.046 \text{ m}^2\text{g}^{-1} \) and required a sample weight of 32.3 g
for the measurements. Hayakawa's isosteric enthalpy measurements
for argon on cubic sodium chloride show a marked increase in value
from \( \theta = 0.7 \) downwards, compared to the more recent measurements of
Jackson and Davis (1974) which start increasing from \( \theta = 0.1 \). The
isosteric enthalpies of Ross and Hinchen (1970) for argon on sodium
bromide only start increasing at \( \theta < 0.1 \) and the isotherm of argon
on sodium chloride indicates a large proportion of homogeneous
surface.

Two methods were chosen for the preparation of high specific
area samples. Both methods depend on the sublimation of the crystal-
line sodium chloride, but differ in the method of collection of the
sodium chloride aerosol. The first procedure uses an electrostatic
precipitator. The second method depends on filtering out the sodium
chloride particles through a microporous filter.

6.3.2 The Preparation by Electrostatic Precipitation

This method has been used by a number of workers including
Keenan and Holmes (1949), Patterson, Morrison and Thompson (1955),
Craig and McIntosh (1952), Young and Morrison (1954), Benson and
Benson (1955).

Ross and Hinchen (1970) have suggested that the presence of
water vapour in the preparation could lead to the hydrolysis of the
sodium chloride surface. However since Ross and Hinchen have shown
that there is no hydrolysis when sodium bromide is exposed to 10 torr pressure of water vapour for 8 hours at 25°C there is no reason to believe that the hydroxide ion will displace the chloride ion in the case of sodium chloride. Craig and McIntosh (1952) have shown that exposure of the electrostatically prepared samples to various relative pressures of water vapour, results in a decrease in the specific surface area of the samples. Moffat and McIntosh (1957) showed that the area decreases to an extent determined by the relative humidity above the sample. This decrease is not dependent on the initial area of the sample or the number of steps or exposures required to reach the final equilibrium. The reason for this behaviour could be that sintering occurs by a process of dissolution at certain parts of the surface and recrystallization takes place to form a surface where no further dissolution can occur without an increase in the ambient relative water vapour pressure.

The apparatus was of the same structure as that used by Waldsax (1970). A silica boat carried the sample in a silica glass tube inside the furnace (see fig. 6.7). The furnace was controlled by a relay and a calibrated chromel-alumel thermocouple. White spot nitrogen was used as the carrier gas and the flow rate measured on a calibrated flow meter. The sodium chloride aerosol first passed through a 1 litre settling chamber and then passed through the vertical precipitator. This consisted of a 3 cm. diameter borosilicate tube with an axial tungsten wire as one electrode and aluminium foil surrounding the length of the tube as the other electrode. The entire system could be evacuated by using an Edward's ED50 rotary pump and nitrogen trap.

The method of preparation for sample 1 consisted of heating the sample in the furnace to 300°C for 6 hours under a vacuum. After
Fig 6.7 Apparatus for the preparation of NaCl by electrostatic precipitation of an aerosol.

Key:
- ▼ cone junction

- ▼ furnace
- ▼ cold trap and rotary pump
- ▼ flowmeter
- ▼ Thermocouple and control unit with DVM
- ▼ collection tube
- ▼ high voltage
- ▼ earthed screen
- ▼ silica boat
- ▼ settling chamber
- ▼ N₂ flow

Apparatus for the preparation of NaCl by electrostatic precipitation of an aerosol.
this time the nitrogen flow was adjusted to 4 litres min\(^{-1}\) and the furnace temperature raised to 820 ± 5°C. The precipitator voltage was adjusted to 15kV and the sample collected. Three separate runs were required to collect 4.009 g of sodium chloride (sample 1). Individual samples were stored in an evacuated silica gel dessicator and after the final collection, immediately placed onto the vacuum frame and degassed.

Sample 1 was a brilliant white colour and showed no signs of a blue hue mentioned by van Zeggeren and Schreiber (1956). It is known that sodium nitrate and sodium nitrite can be formed during the electrostatic precipitation of the aerosol. van Zeggeren and Schreiber (1956) investigated the percentage nitrate formation relationship to the precipitating voltage and amount of oxygen in the carrier gas. They found that the nitrate formation was smaller the lower the oxygen gas concentration and the lower the precipitating voltage. With a voltage of 8kV and 0.05% oxygen in the carrier gas, the nitrate content should be less than 0.05% resulting in about 30% of the surface molecules as the nitrate. However van Zeggeren and Schreiber state that "X-ray diffraction examination confirmed the presence of sodium nitrate impurity in a number of these (samples)". This indicates that the samples which had produced these lines must have been prepared using high concentrations of oxygen in the carrier gas or high precipitating voltages in order to produce a large enough percentage of nitrate to be detected by this method. Also the nitrate impurity must have been present in the bulk crystalline phase for detection to be possible by X-ray diffraction. With the view of avoiding these uncertainties and to elucidate these problems using ADSEFF, a second method of preparation was also adopted.
6.3.3 Preparation by Filtration

This method of preparation has been adopted by Ross and Hinchen (1970) and by Davis and Jackson (1974). Although both groups used different conditions and apparatus for their preparation, their analysis seem to indicate that the surface of their samples were of good quality and highly homogeneous.

The electrostatic precipitator of fig. 6.7 was replaced by a stainless steel chamber containing a 0.4μm cellulose acetate microporous filter. The procedure described for the electrostatic preparation method of §6.3.2 was repeated for the preparation of sample 2. Two separate runs were required to obtain a total of 0.0474 g of sample.

Since the method used a cold carrier gas, the formation of the aerosol by rapid quenching of the sodium chloride vapour would result in a partially amorphous solid. This has been substantiated by Schuff, Schuff and Gendron (1953) and the work of Jackson and Davis (1974).

6.4 MEASUREMENT AND CALCULATION OF THE ADSORPTION ISOTHERMS

6.4.1 Method of Measurement

The standard volumetric procedure for the measurement of adsorption isotherms was followed (see Ross and Olivier 1964).

The samples were outgassed for 16 hours at 100 C. After this time the capacitance manometers were baked for 45 minutes, allowed to cool for 2 hours, and the vacuum rechecked using the McLeod gauge. The capacitance manometers were then zeroed ready for the measurements to start.

To account for the thermal transpiration effect on the equilibrium pressure and also on the amount of gas adsorbed, three "dead volumes" were calibrated. This was done by using the helium expansion
method. The following volumes were determined:

(i) the volume at 25 C up to the sample tap but excluding the calibrated burettes. This was called the "tube space".

(ii) the volume at 25 C below the sample tap without the nitrogen bath present ($V_2$).

(iii) the volume below the sample tap with the liquid nitrogen bath present and the cold junction maintained at a marked level along the sample tube. This volume is termed the "dead space", $V_d$.

The sample temperature was controlled by the addition of liquid air to the nitrogen bath. This bath was constantly stirred by a motor during all the operations. By measuring the saturation vapour pressure of nitrogen, $P_0$, with the mercury manometer, the bath temperature, $T$ degrees K, could be obtained from the data of Friedman and White (1950) using the equation:

$$\log_{10} P_0 = A + B/T + CT + D\log_{10} T \quad (6.6)$$

where $A$, $B$, $C$ and $D$ are constants.

The gases used for the adsorption were krypton BOC special, X grade, which was 99.99% pure as determined by a mass spectrometric analysis, and BOC special bulk grade argon 99.66% pure with a main impurity, as determined by mass spectrometric analysis, of neon (0.28%).

In the case of the argon isotherms, where pressures greater than 10 torr had to be measured, a back pressure of nitrogen was applied to the reference port of the 145AH-10 head to zero the manometer. In this manner pressures in the range of 10-30 torr could be registered.

When annealing of the sample was undertaken, the procedure was to introduce an atmosphere of dry nitrogen above the sample to a
pressure of 600 torr and then heat the sample to 310-315 C for a predetermined length of time. The temperature was either controlled manually using a variac, or automatically using a chromel-alumel thermocouple in conjunction with a relay control.

6.4.2 Calculation of the Adsorption Isotherm

A knowledge of the "tube space" of the apparatus allows the total number of moles of gas in the system before adsorption to be obtained from the pressure measurements. On adsorption, the "dead space" calibration may be used to determine the number of moles, or volume of gas at STP, that has been adsorbed by the solid. In this work the "ISOTHERM" computer package, HL38, developed by Jaycock and Waldsax (Department of Chemistry, Loughborough University, unpublished) was used for the calculation of the isotherm. A further subroutine was added to the package to correct the data for the effects of thermal transpiration. The final isotherm was expressed in terms of the equilibrium pressure in torr to the amount adsorbed, cm$^3$g$^{-1}$, of gas at STP. Multiplication of this by a factor of 4.464 $\times 10^{-5}$ yields the adsorption in moles g$^{-1}$.

The following points are relevant to this calculation:

(i) As discussed in §6.2, the thermal transpiration effect at the cold junction is important in the case of krypton. It is also important for argon at low pressures. The Liang equation has proved satisfactory for argon (Bennett and Tompkins 1957) using a value of $\phi_g = 2.70$.

The internal diameter of the tube was measured with a cathetometer. To be able to determine the quantity of gas at $P_1$, $T_1$ that was below the cold junction (see fig. 6.8), the volume $V_1$ was required.
(ii) A thermal junction was present at the capacitance manometer measurement ports. The heads were maintained at $49 \pm 0.14 \, ^\circ C$ yielding a Knudsen constant, $R_m$, of 0.962. This problem could have been overcome by using the heads without their integral heaters and relying on the thermostated cabinet. This would have meant recalibrating the heads and also accepting a loss in accuracy, $\approx 0.5\%$, associated with running the heads at a lower temperature. It was also discovered that when the heads were held at a constant pressure with krypton, the pressure stability was far better when the integral heaters were operating. This may have been because of local temperature variations in the cabinet or internal heating effects in the head.

The maximum thermal transpiration error as expressed by Knudsen's equation is $4\%$. This equation has been used by Loriot and Moran (1975), although they are ambiguous over the pressure range they expect it to apply, it does appear a useful means of correction between $2 \times 10^{-4}$ and $5 \times 10^{-6}$ torr. Since the lowest pressure in this work is $\approx 2 \times 10^{-3}$ torr, the error must be considerably less. The

$$v_1 = \frac{V_a - V_3}{T_2 - T_1} \times T_1 \quad (6.7)$$
problem of making a correction is difficult because the thermal junction is along the metal exit port. The parameters that have been determined for the Liang equation with a glass junction are not applicable. The metal junction is expected to be more diffuse and could possibly lead to a larger pressure differential (Los and Ferguson 1952).

To detect this thermal transpiration effect a dose of krypton was introduced into a closed volume connected to a McLeod gauge and a capacitance manometer. A series of pressure measurements in the range of 0.1 torr to $3 \times 10^{-3}$ torr were made. Each McLeod pressure reading was repeated three times and the mean compared to the value from the capacitance manometer. Since the maximum deviation was 2.5% at the lowest pressure, no correction for this thermal transpiration effect was made.

(iii) Corrections for the non-ideality of krypton and argon were made using the low pressure form of the Berthelot equation. As reported by Sidebottom (1967), this correction is small, amounting to only 0.0055% in the extreme cases when the saturated vapour pressure of krypton was reached. The correction is larger at pressures obtained in McLeod compression volumes.

(iv) A number of researchers have been concerned with the possibility of correction for mercury drag effects. Takaishi (1965) reported mercury vapour streaming from a McLeod gauge to a cold trap. Sidebottom (1967) was unable to detect the effect in his apparatus when using helium gas. The effect becomes larger with increasing atomic radius of the gas atoms and is also critically dependent on the room temperature and the tube diameter connecting the mercury to the cold trap. The effect of distance between the cold trap and the mercury reservoir (Takaishi and Sensui 1970) is less marked. In the
present vacuum system, the mercury drag effect could only occur between the sample tube and the gas burettes. The work of Takaishi and Sensui (1970) indicates that when using xenon gas, with 2mm.
diameter connecting tubes, errors as large as 10% could result in
the region of $10^{-2}$ torr. This result is obtained from an extrapolation from the work of Takaishi and Sensui (1970) since they used connecting capillaries of 7.55mm. diameter. The effect is expected
to be smaller for krypton and argon. This was investigated by
allowing pressure equilibrium to be obtained with the sample tap
open and the pressure changes measured when the tap was closed.
Since no changes occurred over the entire pressure range used in
the adsorption measurement for krypton, the effect was assumed to be negligible and no corrections for this effect were made.
7.1 THE EXPERIMENTAL ISOTHERMS

7.1.1 Introduction

The isotherms were determined by the methods discussed in §6.4. They are listed in Table 7.1 according to the adsorbate gas that was used in the measurements, the method of preparation of the two samples and their subsequent heat treatment. Sample 1 was prepared by electrostatic precipitation of a sodium chloride aerosol and sample 2 by filtration of a similar aerosol. If annealing was carried out, this was done at a temperature of 310-315 C in an atmosphere of dry nitrogen at 600 torr pressure.

TABLE 7.1 SPECIFICATION OF THE ADSORPTION ISOTHERMS

elec. : the sample was prepared by the method of electrostatic precipitation of the aerosol.

fil. : the sample was prepared by the filtration of the aerosol.

<table>
<thead>
<tr>
<th>sample number</th>
<th>isotherm label</th>
<th>figure</th>
<th>gas</th>
<th>temperature /K</th>
<th>prep. method</th>
<th>annealing time /hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>7.1</td>
<td>krypton</td>
<td>77.5</td>
<td>elec.</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1b</td>
<td>7.5</td>
<td>argon</td>
<td>76.1</td>
<td>elec.</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1c</td>
<td>7.5</td>
<td>argon</td>
<td>76.1</td>
<td>elec.</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1d</td>
<td>7.5, 7.6</td>
<td>argon</td>
<td>76.1</td>
<td>elec.</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>7.3</td>
<td>krypton</td>
<td>76.1</td>
<td>fil.</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>7.3</td>
<td>krypton</td>
<td>76.1</td>
<td>fil.</td>
<td>21</td>
</tr>
</tbody>
</table>
Fig. 7.1a Isotherm (la) for the adsorption of krypton at 77.5K on electrostatically prepared sodium chloride

Key: • Experimental points

$p_0 = 1.78$ torr
Fig. 7.1b. Isotherm (1a) at low pressures

Volume adsorbed / cm³ (at STP) g⁻¹

P/torr
Fig. 7.2 Electronmicrograph of the particles of sample 1 after 6 hours annealing.
7.1.2 Isotherm (la)

This isotherm is presented in figs 7.1a and b and clearly shows the "step" that is associated with the two-dimensional condensation of krypton on the (100) face of sodium chloride. Hence it can be seen that at 77.5K krypton is below its two-dimensional critical temperature, $T^{2D}$. This result is not altogether expected on the basis of the experimental values of the ratio of $T^{2D}$ to the three-dimensional critical temperature, $T^{3D}$, shown in Table 7.2.

It is observed that the values of $T^{2D}/T^{3D}$ obtained from the van der Waals' model and the virial expansion, which are also shown in Table 7.2, are higher than those values obtained experimentally.

<table>
<thead>
<tr>
<th>gas</th>
<th>adsorbent</th>
<th>method</th>
<th>$T^{2D}/T^{3D}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>NaCl</td>
<td>experimental</td>
<td>0.36</td>
<td>Ross and Clark (1954)</td>
</tr>
<tr>
<td>Kr</td>
<td>NaBr</td>
<td>experimental</td>
<td>0.37</td>
<td>Ross and Winkler (1955)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(a)</td>
<td>0.50</td>
<td>Hill (1960)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b)</td>
<td>0.46</td>
<td>Morrison and Ross (1973)</td>
</tr>
</tbody>
</table>

de Boer (1953) has attributed this difference between the experimental and theoretical values to the effects of the
induced dipole self-interaction of the xenon and krypton atoms above the ionic surface. However, the results in §4.7.3 indicate that this is not likely and that the effects of the symmetry and topology of the adsorption potential field above the ionic surface, as discussed in §4.6, are more important. The values of $T^2_{2D}$ obtained by using $T^2_{2D}/T^3_{3D} = 0.37$ are 55.8K for argon and 77.5K for krypton, thus indicating that $T^2_{2D}/T^3_{3D} > 0.37$, and that argon at 77.5K is above its two-dimensional critical temperature.

Figure 7.1a also shows that the "step" at a pressure of 0.29 torr is almost vertical thus indicating the high degree of homogeneity of the (100) surfaces of the sodium chloride crystals. The particles of sample 1, prepared with 6 hours annealing, are seen to be approximately cubic (fig. 7.2) with a number of heterogeneities present such as high index planes exposed at the corners of the cubes and small "pits" in the surface of the cubes. As will be described in §7.2.2, further heat treatment of the sample did not affect its adsorption characteristics.

The saturation vapour pressure of solid krypton was determined by measuring the adsorption isotherm above the monolayer region. This resulted in a steep rise in the volume of gas adsorbed at a pressure of 1.78 torr at 77.50K. This is in between the values quoted by Sidebottom (1967) i.e. $P_0 = 1.76$ torr at 77.49K and that of Keesom, Mazur and Meihuizen (1935), i.e. $P_0 = 1.80$ torr at 77.49K.

The low pressure region of the adsorption isotherm was determined in detail as shown in fig. 7.1b, so that the analysis by ADSEFF could be accomplished over a wide range of adsorption energies.

7.1.3 Isotherms (2a) and (2b)

The discussion of §6.3.2 indicated that there was some doubt about the purity of samples prepared by the method of electrostatic
Fig. 7.3a The adsorption isotherms (2a) and (2b) at 76.1K for krypton on filtered sodium chloride

Key: • Experimental points obtained before annealing
  ○ Experimental points after 21 hours annealing

Volume adsorbed / cm$^3$ (at STP) g$^{-1}$

$p$/torr

0 0.2 0.4 0.6 0.8 1.0
Fig. 7.3b Isotherm (2b) at low pressures
Fig. 7.4 Comparison of isotherms (1a), (2b) and the isotherm determined by Ross and Hinchen (1970)

Key: 
- - Ross and Hinchen (1970) [left ordinate]
--- isotherm (1a) [right ordinate]
• isotherm (2b) [left ordinate]
precipitation. Isotherms (2a) and (2b) were measured to ascertain the differences between samples 1 and 2.

The isotherms are presented in fig. 7.3. Isotherm (2a) obtained by adsorption on sample 2 before annealing, has a much smaller "step" than might be expected from a comparison with isotherm (1a). However after annealing the resulting isotherm (2b) showed an increase in "step" length of about 49% and remained unchanged with further heating. The "step" of the isotherm (2b) occurs at a pressure of 0.28 torr which is slightly smaller than the value obtained for isotherm (1a), because the adsorption temperature is lower. There is also a slight shift in the "step" position, (0.01 torr), obtained after the sample was annealed.

A comparison of isotherms (1a) and (2b) by plotting the adsorption volume per unit mass of sample on a logarithmic scale (fig. 7.4), indicates that by accounting for the difference in the specific surface area of the two samples, i.e. by translating the \( \ln V \) axis, the two isotherms are almost identical. This shows that the criticism by Ross and Hinchen (1970) and van Zeggeren and Schreiber (1956) about the electrostatic precipitation method is not valid for the conditions of preparation used in this experiment. This point will be mentioned again in the ADSEFF analysis of isotherms (1a) and (2b) (see §7.2.1).

7.1.4 Isotherms (1b), (1c) and (1d)

The three isotherms for the adsorption of argon on sodium chloride are shown in fig. 7.5 and correspond to different annealing times. The difference between isotherms (1b) and (1c) is clearly evident and shows that sintering occurred, accompanied by some process that gave rise to a steepening of the isotherm. After a total of 100 hours heating, the derived isotherm (1d) was coincident with isotherm (1c) and showed no reduction in specific surface area.
Fig. 7.5 The adsorption isotherms (1b), (1c) and (1d) at 76.1K for argon on electrostatically prepared sodium chloride

Key:
- ● sample not annealed
- ○ sample annealed for 6 hours
- □ sample annealed for 100 hours
Fig. 7.6 The low pressure region of the adsorption isotherm (1d) for argon adsorbed at 76.1K on electrostatically prepared sodium chloride.

Key:
- experimental points
- residual isotherm
- analysis (1) §7.3.3
- analysis (2) §7.3.3
Jackson and Davis (1974) obtained similar results although they annealed for 120 hours and subsequently for a further 24 hours. The second heating only resulted in a reduction in the specific surface area of the sample which may be attributed to the higher specific area of their sample compared to sample 1.

The low pressure region of isotherm (1d) was measured in detail and some of the points are shown in fig. 7.6. This will be used in the virial analysis to compare with the theoretical results that were obtained in Chapter 4.

7.2 ANALYSIS OF THE ADSORPTION ISOTHERMS BY ADSEFF

7.2.1 Analysis of the Krypton Isotherms (1a), (2a) and (2b)

The use of ADSEFF to determine the heterogeneity of surfaces from adsorption isotherm measurements has been described in Chapter 5. The algorithm can be applied when the isotherm exhibits "steps" and is used here to analyse the krypton data to determine the heterogeneity of sample 2, before and after annealing, and also to determine the difference between samples 1 and 2.

Table 7.3 collects the parameters that were used in the analysis of the isotherms.

Isotherm (1a) was analysed by using the HdB and the FG model isotherm equations and isotherms (2a) and (2b) were analysed by using the HdB model isotherm. The C values for the HdB equation were obtained from (5.11), i.e. $C = 2a/kT_\beta$, by using the ideal values of $\alpha$ and $\beta$ (see §5.2.1). In the case of the FG equation, C was obtained from (5.28) by using $2a = \frac{1}{2} \times$ (heat of sublimation of krypton). The heat of sublimation (2.658 kcal mol$^{-1}$) was taken from Fisher and McMillan (1958). It was found that changes in C of less than 5% only translated the energy axis of the final distribution, but that larger
changes did have significant affects on the shape of the distribution function. Errors in the estimate of \( \ln A^0 \) would also have the affect of translating the energy axis without altering the shape of the distribution curve.

**TABLE 7.3** PARAMETERS THAT WERE USED IN THE ADSEFF ANALYSIS OF ISOTHERMS 1a, 2a AND 2b

<table>
<thead>
<tr>
<th>isotherm</th>
<th>mod.</th>
<th>( \theta_l )</th>
<th>( \theta_h )</th>
<th>( (P/K)_{\text{step}} )</th>
<th>( \ln A^0 )</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>HdB</td>
<td>0.05609088</td>
<td>0.6864110</td>
<td>0.03705245</td>
<td>14.632</td>
<td>9.10</td>
</tr>
<tr>
<td>1a</td>
<td>FG</td>
<td>0.2745070</td>
<td>0.7259430</td>
<td>0.1159032</td>
<td>13.6998</td>
<td>4.31</td>
</tr>
<tr>
<td>2a</td>
<td>HdB</td>
<td>0.05328765</td>
<td>0.6918192</td>
<td>0.03647055</td>
<td>14.623</td>
<td>9.20</td>
</tr>
<tr>
<td>2b</td>
<td>HdB</td>
<td>0.05328765</td>
<td>0.6918192</td>
<td>0.03647055</td>
<td>14.623</td>
<td>9.20</td>
</tr>
</tbody>
</table>

The range of adsorption data input to ADSEFF in all cases was 0.002 torr \( \leq P \leq 1.4 \) torr which was covered by a total of 80 points. Subroutine DATASET was used in the analysis and subroutine SMOOTH was also incorporated although the final result was found to be the same whether it was included or not. Care was taken to ensure that there were at least 10 points on the isotherm "step" and a large number of points at the "step" limits, so that an accurate representation by the cubic splines was obtained (see §5.4.3).
Fig. 7.7 Results of the analysis by ADSEFF on isotherm (1a)

Key:
- • using the FG model
- o using the HdB model

isotherm function

max. $F' = 75$

max. $F' = 35$

$u$ (kcal mol$^{-1}$)
Fig. 7.8 The site energy distribution function obtained by ADSEP from the analysis of the adsorption of krypton on sodium chloride at 76.1K

Key:
- \( \times \) - isotherm (2a)
- \( \circ \) - isotherm (2b)
The results of the analysis are shown in Table 7.4 and the distribution functions that were determined by ADSEFF are illustrated in figs. 7.7 and 7.8.

### Table 7.4: The Results of the Analysis of Isotherms 1a, 2a, and 2b by ADSEFF

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Cycles</th>
<th>r.m.s.</th>
<th>$V_m$ /cm$^3$(STP) g$^{-1}$</th>
<th>Mod.</th>
<th>Peak Position /kcal. mol$^{-1}$</th>
<th>Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>11</td>
<td>0.027</td>
<td>0.578</td>
<td>HdB</td>
<td>1.94</td>
<td>7.7</td>
</tr>
<tr>
<td>1a</td>
<td>9</td>
<td>0.032</td>
<td>0.488</td>
<td>FG</td>
<td>1.97</td>
<td>7.7</td>
</tr>
<tr>
<td>2a</td>
<td>3</td>
<td>0.027</td>
<td>2.023</td>
<td>HdB</td>
<td>1.89</td>
<td>7.8</td>
</tr>
<tr>
<td>2b</td>
<td>6</td>
<td>0.034</td>
<td>1.850</td>
<td>HdB</td>
<td>1.90</td>
<td>7.8</td>
</tr>
</tbody>
</table>

The difference between the experimental isotherms and the isotherms generated by using the final distribution functions was less than the experimental error (a maximum of 5% in the volume adsorbed (at STP)g$^{-1}$ at the lowest pressures measured).

The close similarity between the distribution functions obtained from (1a) and (2b) [see figs 7.7 and 7.8] using the HdB model isotherm function in the analysis is obvious, and confirms the conclusion that the samples are very similar and there was no appreciable contamination of the sodium chloride during the preparation of sample 1.

The analysis of isotherm (1a) by using the FG model isotherm equation, leads to a distribution function (fig. 7.7) showing less

---

HdB - Hill-de Boer equation §5.2.1
FG - Fowler-Guggenheim equation §5.2.3.

$V_m$ - Normalizing volume discussed in §5.4.1
heterogeneities on the surface of sample 1 than is indicated by the HdB analysis. This result is expected from the previous work by House and Jaycock (1974a) who analysed the adsorption isotherm of krypton on anatase (TiO₂) by using the Langmuir and the HdB model isotherm functions. The analysis using the Langmuir equation gave a larger main peak on the distribution function than the corresponding peak obtained when the HdB model isotherm was adopted.

An examination of the distribution functions shown in fig. 7.7 in the region below an adsorption energy of 1.9 kcals mol⁻¹, reveals two peaks on both the distributions. In the case of the distribution function derived using the PG equation, one of these peaks represents the main source of surface heterogeneities. The final sharp increase in F' near 1.7 kcals mol⁻¹ is due to multilayer adsorption, so that the proceeding minimum is the lowest adsorption energy on the uncovered surface that can be determined before the onset of multilayer adsorption. This behaviour also occurs with the HdB derived functions but the distribution function is only obtained up to the proceeding minimum as shown in fig. 7.7 and 7.8. This means that the normalizing volume, Vₘ, presented in Table 7.4 may be interpreted as the monolayer volume provided there is not an appreciable number of low energy sites. However caution is required in this interpretation because when the arbitrary multilayer correction, explained in §5.4.1, is applied to isotherm (1a), the F' values for U < 1.9 kcals. mol⁻¹ are zero and so the corresponding Vₘ value ( = 0.400 cm³(STP g⁻¹), is lower.

The changes in adsorption energy with annealing sample 2 are clearly visible on an examination of fig. 7.8. The higher energy sites are reduced in frequency and the main peak height increases two fold. The lower energy sites are also less abundant but still appear as two separate peaks. The change in the Vₘ value presented
in Table 7.4, also reflects the reduction in the specific surface area that occurs with annealing.

The values of the peak position shown in Table 7.4 correspond to the adsorption energy, \( U \), for the krypton atom on the (100) surface. This adsorption energy is related to the maximum adsorption energy, \( U^0 \), calculated in Chapter 3, by

\[
U^0 = U + \varepsilon_0^{\text{vib}}
\]

(7.1)

where \( \varepsilon_0^{\text{vib}} \) is the zero state vibrational energy of the adsorbed atom. In the case of krypton on sodium chloride, the limiting calculations discussed in §3.5 and §3.6 indicate a vibrational frequency in the range \( (0.75 - 1.06) \times 10^{12} \text{ s}^{-1} \). Hence using the simple harmonic approximation, \( \varepsilon_0^{\text{vib}} \) should lie within the range \( 0.036 \pm 0.051 \text{ kcals. mol}^{-1} \). Hence for the HdB model, the analysis gives \( U^0 = 1.96 \pm 0.03 \text{ kcals. mol}^{-1} \) (8.20 ± 0.13 kJ mol \(^{-1} \)) and for the FG model, \( U^0 = 2.02 \text{ kcals. mol}^{-1} \) (8.45 kJ mol \(^{-1} \)). These values lie between the maximum adsorption energies shown in Table 3.1 and Table 3.9 which correspond to the calculation using the FW approximation for the unrelaxed surface and that using the Mayer dispersion constant for the ions for the relaxed and unrelaxed surfaces as discussed in §3.6.

If the Ross and Olivier (1964) analysis is performed on isotherm (1a) as outlined in §5.3, the step may be described by a \( \gamma = \infty \) step function with an adsorption energy, \( U \), of 1.94 kcals. mol \(^{-1} \) and adsorption volume of 0.379 cm \(^3\) (at STP)g \(^{-1} \). If the adsorption due to this homotactic area is subtracted from the total adsorption isotherm, the remaining adsorption points may be analysed using the same Ross and Olivier (1964) procedure. There is some difficulty in fitting the \( \ln(P/K) \) versus \( \theta \) plot to the corresponding \( \ln P \) versus \( \ln V \) graph since more than one set of Gaussian parameters may be obtained, depending
where multilayer adsorption is assumed to begin. Two sets of parameters were distinguished; a $\gamma = 3$ Gaussian with $U' = 2.015$ kcals. mol.$^{-1}$ and $V_m = 0.126 \text{ cm}^3 (\text{at STP}) g^{-1}$, and a $\gamma = 5$ with $U' = 2.185$ kcals. mol.$^{-1}$ and $V_m = 0.091 \text{ cm}^3 (\text{at STP}) g^{-1}$. There is little difference between these distributions and they both indicate heterogeneities of the region of 19-26% of the surface and total $V_m$ values of 0.470 and 0.505 cm$^3 (\text{at STP}) g^{-1}$ respectively.

One of the ambiguities associated with the analysis of "step" isotherms by the Ross and Olivier (1964) analysis is fitting the "step" region to the generated isotherms since unless the "step" is exactly perpendicular and the "turning points" at the "step" limits are sharp, information is generally lost concerning the distribution function near to the main peak position.

7.2.2 Analysis of the Argon Isotherms (lb) and (ld)

Since argon is below its two-dimensional critical temperature, the initial "step" function used to determine the range of adsorption energies in ADSEFF is constructed such that it passes through the point of inflection of the model isotherm. The corresponding $(P/K)_\text{step}$ may then be determined by substituting back into the appropriate model isotherm function. The parameters that were used here are collected in Table 7.5.

The results of the ADSEFF analysis of the argon adsorption isotherms obtained before and after the sample was annealed (isotherms (lb) and (ld)), are shown in figs. 7.9 and 7.10. The important parameters obtained from this analysis are listed in Table 7.6.

Figure 7.9 clearly shows the effect of annealing on the site energy distribution function obtained by using the H&B model isotherm function in the ADSEFF analysis. The higher energy adsorption sites are reduced in frequency, the 4 small peaks being effectively removed.
Fig. 7.9 The site energy distribution function obtained by ADSEFF from the HdB analysis of the adsorption of argon on sodium chloride.

Key: 
- isotherm (lb)
- isotherm (ld)
Fig. 7.10 The site energy distribution function obtained by ADSEFF from the FG analysis of the adsorption of argon on sodium chloride at 76.1K

Key:
- $\times$ isotherm (lb)
- $\circ$ isotherm (ld)
The frequency of the sites giving rise to the main peak is also increased with annealing. A similar result is obtained by using the FG model isotherm in the analysis, with the 4 peaks at high adsorption energies disappearing and the main peak height increasing. A comparison of fig. 7.9 and 7.10 substantiates the conclusions drawn from the analysis of the krypton isotherm (1a), (§7.2.1), that the FG model isotherm function used in ADSEFF leads to a distribution function that implies a more homogeneous surface.

**TABLE 7.5** Parameters that were used in the ADSEFF analysis of Argon isotherms (1b) and (1d)

<table>
<thead>
<tr>
<th>Model</th>
<th>Model Isotherm Constants</th>
<th>( \theta_1 )</th>
<th>((P/K)_{step})</th>
<th>( \ln A^0 )</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HdB</td>
<td>FG</td>
<td>0.3331753</td>
<td>0.0904318</td>
<td>14.386</td>
<td>6.63</td>
</tr>
<tr>
<td>FG</td>
<td></td>
<td>0.50</td>
<td>0.21440</td>
<td>13.938</td>
<td>3.08</td>
</tr>
</tbody>
</table>

The \( V_m \) values presented in Table 7.6 do not correspond to a monolayer volume since the adsorption patches of energy \( U < 1.35 \) kcals. mol\(^{-1}\) are not included in the distribution because the isotherm data range was not sufficient, because of the difficulties of measuring the higher pressure part of the isotherm with a 10 torr F.S.D. Baratron.
TABLE 7.6 THE RESULTS OF THE ANALYSIS OF ISOTHERMS (lb) AND (ld) BY ADGEFF

HdB - Hill-de Boer equation §5.2.1
FG - Fowler-Guggenheim equation §5.2.3.

V_m - Normalizing volume discussed in §5.4.1

<table>
<thead>
<tr>
<th>isotherm</th>
<th>cycles</th>
<th>r.m.s.</th>
<th>V_m/cm³(STP)</th>
<th>mod.</th>
<th>peak position/kcals. mol⁻¹</th>
<th>fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>lb</td>
<td>19</td>
<td>0.003</td>
<td>0.301</td>
<td>HdB</td>
<td>1.39</td>
<td>7.9</td>
</tr>
<tr>
<td>ld</td>
<td>17</td>
<td>0.003</td>
<td>0.283</td>
<td>HdB</td>
<td>1.38</td>
<td>7.9</td>
</tr>
<tr>
<td>lb</td>
<td>20</td>
<td>0.014</td>
<td>0.244</td>
<td>FG</td>
<td>1.45</td>
<td>7.10</td>
</tr>
<tr>
<td>ld</td>
<td>20</td>
<td>0.015</td>
<td>0.235</td>
<td>FG</td>
<td>1.44</td>
<td>7.10</td>
</tr>
</tbody>
</table>
TABLE 7.7 COMPARISON OF THE RESULTS OF THE CALCULATION OF U FOR ARGON ON SODIUM CHLORIDE USING THE FW APPROXIMATION, MODELS A, B AND C (see §4.3.5 and §3.5), FOR THE DETERMINATION OF THE GAS-SOLID POTENTIAL ENERGY FIELD

key:  
\( r \) - Relaxed (100) surface  
\( ur \) - Unrelaxed (100) surface

<table>
<thead>
<tr>
<th>model</th>
<th>surface</th>
<th>( U^0 ) /kcal/mol(^{-1})</th>
<th>( v^1 ) /10(^{12})s(^{-1})</th>
<th>( E_{\text{vib}}^0 ) /kcal/mol(^{-1})</th>
<th>( U ) /kcal/mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FW</td>
<td>ur</td>
<td>1.72</td>
<td>1.42</td>
<td>0.07</td>
<td>1.65</td>
</tr>
<tr>
<td>A</td>
<td>r</td>
<td>1.11</td>
<td>1.11</td>
<td>0.05</td>
<td>1.06</td>
</tr>
<tr>
<td>B</td>
<td>ur</td>
<td>1.27</td>
<td>1.12</td>
<td>0.05</td>
<td>1.22</td>
</tr>
<tr>
<td>B</td>
<td>r</td>
<td>1.36</td>
<td>1.19</td>
<td>0.06</td>
<td>1.30</td>
</tr>
<tr>
<td>C</td>
<td>ur</td>
<td>1.84</td>
<td>1.34</td>
<td>0.09</td>
<td>1.75</td>
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<tr>
<td>C</td>
<td>r</td>
<td>1.96</td>
<td>1.40</td>
<td>0.07</td>
<td>1.89</td>
</tr>
</tbody>
</table>
The peak positions shown in Table 7.6 which correspond to the adsorption energy, \( U \), of argon on (100) sodium chloride, are again between the values obtained using the \( \text{FW} \) approximation and model A (§4.3.5) in the determination of the potential energy field. The \( U^0 \) values shown in Table 7.7 are the maximum adsorption energy values, \( U^0(x^0,y^0,z^0) \), and are strictly only applicable if the FG model applies, i.e. the adsorbate is localized. The comparison of the zero coverage isosteric enthalpies in Table 4.9 showed that best agreement between theory and experimental results was for a potential model between B and C (see §4.3.5). This indicates that the adsorbate is in the region of the localized to mobile transition and hence it is more meaningful to compare isosteric enthalpies rather than adsorption energies because the isosteric enthalpy includes a contribution due to lateral motion. However, the present results do agree with the conclusion drawn from the isosteric enthalpy comparison, since the \( U \) values in Table 7.6 are between the values obtained from potential models B and C in Table 7.7.

7.3 THE VIRIAL ANALYSIS OF THE ADSORPTION ISOTHERM (1d)

7.3.1 Introduction

As discussed above, the determined degree of heterogeneity of sample 1, after annealing, depends upon the model isotherm used in the analysis. For krypton adsorption, the results of the calculations in Chapter 3 indicate that the adsorbate is likely to be largely localized. Hence if the FG equation is adopted, the frequency of higher energy patches, i.e. \( U > 2.0 \text{ kca}ls. \text{ mol}^{-1} \), is low (see fig. 7.7). This is also found to be the case with the argon isotherm analysis, fig. 7.10, although the results of Chapter 3 indicated that argon is expected to be more mobile than krypton. Using this
result the initial "knee" on the low pressure argon adsorption isotherm shown in fig. 7.6 may be ascribed to adsorption on the high energy sites. This is equivalent to the procedure used by Ross and Hinchen (1970) to determine the surface heterogeneity of their sodium chloride sample. The patches with energies less than the main peak energy will not contribute significantly to the adsorption isotherm at low pressures, i.e. in the region shown in fig. 7.6. Within this limitation, it is possible to construct a residual isotherm by subtracting the adsorption due to the heterogeneities as determined by the linear extrapolation of the experimental isotherm to the adsorption volume axis. The residual isotherm (see fig. 7.6) may then be ascribed to the adsorption of argon on the (100) surface. In the case of the low pressure region of the krypton isotherm (1a) shown in fig. 7.1b, the adsorption volume at the intercept corresponds to 3% of the monolayer volume \( V_m = 0.488 \text{ cm}^3 \) (at STP) \( g^{-1} \) from Table 7.4.

The residual isotherm may now be analysed using the two-dimensional virial equation discussed in Chapter 4. However, before this can be carried out, the surface area of the adsorbent is required. In the present context this may be interpreted as the specific surface area, \( A \), (surface area per gram of adsorbent) which can be determined from the adsorption volume, expressed in \( \text{cm}^3 \) (STP) \( g^{-1} \), if some estimate of the adsorption cross-section is available.

7.3.2 The Determination of the Specific Surface Area of Sample 1

The specific surface area, \( A \), may be calculated from the relationship:

\[
A = 2.689 \times 10^3 \frac{V_m \sigma_m}{n^2} \text{ } g^{-1}
\]  

(7.2)
where: \( V_m \) is the monolayer volume (\( \text{cm}^3(\text{STP})g^{-1} \))

\( \sigma_m \) is the area per atom, \( (\text{Å}^2) \), when the monolayer compression is a maximum

Two problems now exist in the evaluation of \( A \):

(i) The determination of the \( V_m \) value. The analysis of the krypton isotherms in §7.2.1 showed that this is not only dependent upon the choice of the model isotherm adopted in ADSEFF but also upon the amount of multilayer adsorption occurring on the higher energy patches, i.e. it may be postulated that the 2 peaks in fig. 7.8 at \( U < 1.9 \text{ kcal mol}^{-1} \) are due to multilayer adsorption.

(ii) The correct choice of the value of \( \sigma_m \). This problem has been discussed by Sidebottom (1967) and Gregg and Sing (1967), both quoting values within a range: \( 14.6 - 24.2 \text{ Å}^2 \text{ atom}^{-1} \).

In the present work the use of the FG model isotherm in ADSEFF to analyse isotherm (la) led to a \( V_m = 0.488 \text{ cm}^3(\text{STP})g^{-1} \) (Table 7.4). The adsorption site area becomes equal to the limiting area per atom, \( \sigma_m \), i.e. \( \sigma_m = \frac{a^2}{2.0} \) where 'a' is the lattice period in Angstroms.

Hence in the case of (100) sodium chloride, \( \sigma_m = 15.9 \text{ Å}^2 \), and applying (7.2) yields a value of \( A = 2.09 \text{ m}^2\text{ g}^{-1} \).

Alternatively, if in spite of the discussion in Chapters 3 and 4, the results of the ADSEFF analysis with the HdB equation are accepted, then by using the liquid density \( \sigma_m \) value, i.e. \( \sigma_m = 15.2 \text{ Å}^2 \), a value of \( A = 2.36 \text{ m}^2\text{ g}^{-1} \) is obtained. Only when the arbitrary multilayer correction (§5.4.1) is applied does the value decrease to 1.66 \( \text{ m}^2\text{ g}^{-1} \).

The Ross and Olivier (1964) analysis (§7.2.1) also indicates a high specific surface area in the range of \( 2.06 - 2.61 \text{ m}^2\text{ g}^{-1} \).

This confused situation may be further investigated by applying Gibb's adsorption theorem, (see Ross and Olivier 1964), to the
krypton isotherm (1a). This theorem may be written in the form:

$$\pi = \frac{kT}{\sigma} \int_{0}^{P} \sigma d\ln P$$  \hspace{1cm} (7.3)

where: \( \pi \) - the two-dimensional (spreading) pressure
\( \theta \) - the fraction of monolayer coverage

This may be rewritten:

$$\pi = kT \int_{0}^{P} \frac{1}{\sigma} d\ln P$$  \hspace{1cm} (7.4)

where \( \sigma \) is the surface area per atom at the equilibrium pressure, \( P \).

The two-dimensional (spreading) pressure may be evaluated using:

$$\pi = \frac{RT}{22400 \times 10^4 \Lambda} \int_{0}^{P} V d\ln P$$  \hspace{1cm} (7.5)

where: \( R \) - gas constant
\( V \) - adsorption volume in cm\(^3\) (at STP) g\(^{-1}\)

This corresponds to an area per atom of:

$$\sigma = \frac{A}{V} \times 3.719$$  \hspace{1cm} (7.6)

where: \( \sigma \) is in units of \( \AA^2 \) atom\(^{-1}\)

A graph of \( \pi \) versus \( \sigma \) is presented in fig. 7.11 for \( A = 2.0 \ \text{m}^2 \ \text{g}^{-1} \) and \( A = 2.65 \ \text{m}^2 \ \text{g}^{-1} \). This illustrates that condensation takes place at a two-dimensional pressure of 2.3 dyne cm\(^{-1}\) with \( A = 2.0 \ \text{m}^2 \ \text{g}^{-1} \) or 1.8 dyne cm\(^{-1}\) with \( A = 2.65 \ \text{m}^2 \ \text{g}^{-1} \). Unfortunately there is no criteria to distinguish between the two cases, except that the area per atom at the transition pressure is 21.7 and 29.0 \( \AA^2 \) atom\(^{-1}\) obtained using \( A = 2.0 \) and 2.65 \( \text{m}^2 \ \text{g}^{-1} \) respectively. Since for this system, the lower value of \( \sigma \) is more acceptable this result agrees with the lower
Fig. 7.11 The surface area per atom as a function of the two-dimensional spreading pressure obtained from krypton isotherm (1a)

\[ A = 2.0 \text{ m}^2\text{g}^{-1} \]

\[ A = 2.65 \text{ m}^2\text{g}^{-1} \]
specific surface area obtained using the FG isotherm in ADSEFF.

Finally the electronmicrographs, one of which is shown in fig. 7.2, may be used to determine a surface area by measuring the dimensions of a large number of the cubic crystals and calculating the associated specific surface area. This procedure gave a value of $2.0 \pm 0.4 \text{ m}^2 \text{g}^{-1}$.

Considering the above factors, the value of $A$ obtained from ADSEFF using the FG equation, i.e. $A = 2.09 \text{ m}^2 \text{g}^{-1}$, seems to be the most reliable and is used in the following virial analysis.

7.3.3 The Calculation of $K_H$ and $B_{2D}$ from Isotherm (1d)

The logarithmic form of the two-dimensional virial expansion may be rewritten from (4.26b):

$$
\ln(P/V) = \ln \left[2.017 \times 10^{21}/(K_H A)\right] + 5.377 \times 10^{23} B_{2D} V/A + 1.084 \times 10^{45} C_{2D} V^2/A^2 + \ldots (7.7)
$$

where:
- $P$ - pressure in torr
- $V$ - volume adsorbed in cm$^3$(at STP)$g^{-1}$
- $A$ - specific surface area in cm$^2$g$^{-1}$
- $B_{2D}$ - second two-dimensional virial coefficient in units of m$^2$ atom$^{-1}$
- $C_{2D}$ - third two-dimensional virial coefficient in units of m$^3$ atom$^{-1}$
- $K_H$ - Henry's law constant in units of atom N$^{-1}$

The corresponding isotherm equation is:

$$
P = \frac{V \times 2.017 \times 10^{21}}{K_H A} \exp\left(\frac{5.377 \times 10^{23} B_{2D} V}{A}\right) \times \exp\left(1.084 \times 10^{45} C_{2D} V^2/A^2\right) (7.8)
$$
The contribution of $C_{2D}$ (assuming the value for a structureless surface, §4.5) only becomes apparent in (7.8) for $P > 14$ torr and since the perturbation terms are expected to decrease $C_{2D}$, the third term is not included in the present analysis.

Hence following the method suggested by Everett (1970), the experimental data was plotted as $\ln(P/V)$ versus $V$ as shown in fig. 7.12. Two straight lines were then fitted to this data:

(i) a least-squares line through the entire set of points that are plotted in fig. 7.12 (to be called analysis (1))
(ii) a least-squares line through only the higher adsorption volume points as shown in fig. 7.12 (to be called analysis (2)).

As a result of the linear extrapolation from the "knee" in isotherm (1d) shown in fig. 7.6, the lower pressure region, i.e. $P < 4$ torr, cannot satisfy the logarithmic relationship (7.7). Hence because of the uncertainties associated with this extrapolation, analysis (2) is more reliable.

The results of the analysis are presented in Table 7.8. The corresponding isotherms obtained by plotting (7.8) using the values of $K_H$ and $B_{2D}$ obtained in (i) and (ii) above and with $C_{2D} = 0$, are shown in fig. 7.6.

TABLE 7.8 VALUES OF $K_H$ AND $B_{2D}$ OBTAINED FROM THE VIRIAL ANALYSIS OF THE ARGON ADSORPTION ISOTHERM (1d)

<table>
<thead>
<tr>
<th>analysis</th>
<th>$K_H/10^{13}$ atom $N^{-1}$</th>
<th>$B_{2D}/10^{-20}$ m$^2$ atom$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>37.6</td>
<td>-14.7</td>
</tr>
<tr>
<td>(ii)</td>
<td>31.3</td>
<td>-24.9</td>
</tr>
</tbody>
</table>
Fig. 7.12  Virial analysis of the argon adsorption isotherm (1d)

Key:  
- experimental data
- analysis (1)
- analysis (2)

\[ \ln \frac{P}{V} \]

Volume adsorbed / cm\(^3\)(at STP)g\(^{-1}\)
The difference between the results of the analysis (1) and (2) is less important than their general agreement. These are the first values that have been presented for adsorption on any ionic crystal and their magnitudes are in agreement with the results obtained in Chapter 4. A comparison with Table 4.9 clearly shows that the $K_H$ values in Table 7.8 are in between those calculated using potential models B and C, i.e. $5.3 \times 10^{13}$ atom $N^{-1}$ and $112.5 \times 10^{13}$ atom $N^{-1}$ respectively, and very much larger than the value computed from model A, i.e. $1.73 \times 10^{13}$ atom $N^{-1}$. This substantiates the results of the experimental isosteric enthalpy measurements which were also found to lie between the values predicted using potential models B and C (see Table 4.9).

The two-dimensional second virial coefficient also shows a large difference from the value calculated on a structureless surface, i.e. $-54.1 \times 10^{-20}$ m$^2$ atom$^{-1}$, and from the values obtained using potential model A on an ideal (100) surface ($-61.2 \times 10^{-20}$ m$^2$ atom$^{-1}$) and a relaxed (100) surface ($-42.9 \times 10^{-20}$ m$^2$ atom$^{-1}$). However, potential model C gave a value of $-17.9 \times 10^{-20}$ m$^2$ atom$^{-1}$ for the adsorption of argon at 77.5K on a relaxed (100) surface. This lower value is in good agreement with the values presented in Table 7.8, although this is probably fortuitous since no account has been taken of a possible third-body effect in this calculation. The third-body effect would also decrease the value of $B_{2D}$ and since a potential model between B and C would yield a higher $B_{2D}$ value, the third-body effect would be required to obtain agreement with experimental determinations. This problem requires a more detailed study, but the present results do show that the computation of $B_{2D}$ must include the gas-solid perturbation terms if a complete understanding of the interfacial region is to be obtained by this method.
7.4 Future Work

The application of the gas-solid virial series presented here is a powerful means of investigating the interfacial region. However, a number of theoretical problems still exist if a more complete understanding of a simple system such as argon adsorbed on (100) sodium chloride is to be obtained. These problems, that have already been discussed in Chapters 2, 3 and 4, require further investigation.

From an experimental viewpoint, work has already been started. A new ultra high vacuum (UHV) system has been designed which is an all metal system and excludes mercury burettes. The pumping system consists of a mercury diffusion pump backed by a rotary pump, both isolated from the metal working chamber by a liquid nitrogen trap. A final evacuation to $10^{-9}$ torr should be achieved by isolating the roughing pumps at a pressure of $10^{-3}$ torr, and engaging an ion pump which is attached to the metal working chamber. The Baratron manometers described in Chapter 6 will be used to register the gas pressures. By using this new system, then apart from removing all the complications due to the presence of mercury vapour, the sample may be outgassed to a lower pressure and hence cleaner surface state. This should result in more accurate low pressure isotherm measurements.

The development of ADSEFF should now enable investigation of the heterogeneity of alkali halide crystals prepared by different methods. The smaller the low pressure "knee" obtained due to the adsorption on high energy heterogeneities, the more reliable the corresponding virial analysis.

Finally, for the argon-sodium chloride system in particular, extensive calculations of $B_{2D}$ over a temperature range are required. These should be accompanied by the measurement of adsorption isotherms over a similar range of temperatures to determine values of $K_H$, $q_0$, and $B_{2D}$. 
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Papers published in international journals by the author and supervisor, Dr. M. J. Jaycock, during the period of this work:

1. J. Colloid and Interfac. Sci., 1974, 47, 50
   Title: A Study of the Surface Heterogeneity of an Anatase Sample

   Title: Calculation of the Interaction of Adsorption of Inert Gas on to the (100) Face of Sodium Chloride and Argon on to the (100) Face of Potassium Chloride

   Title: Calculation of the Adsorption Interaction of Argon and Krypton on the Relaxed (100) Faces of Sodium Chloride and Potassium Chloride

   Title: Correct Estimation of Thermal Transpiration Effect of Krypton

   Title: The Application of the Gas-Solid Virial Expansion to Argon Adsorbed on the (100) Face of Sodium Chloride
ABBREVIATIONS

FW  Frost and Woodson
ht  hindered translation
KM  Kirkwood-Miller
LJ  Lennard-Jones
SK  Slater-Kirkwood
SP  Sherwood and Prausnitz
TP  Toxvaerd and Praestgaard