QUANTUM TRANSITION CALCULATIONS FOR GAS-SURFACE INTERACTIONS

by

A. E. Sisson

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SUMMARY

It is first shown that the interaction potential between a gas atom and a solid surface with a finite temperature can be conveniently represented by a two-dimension Fourier series with the coefficients being functions of the distance between the atom and the surface*. This representation is useful and shows the basis for the one-dimensional assumption used in the hard and soft-cube models. Secondly the quantum mechanical analogs of the hard and soft-cube models are used to calculate the probabilities for multiple phonon transitions for the gas-surface collisions. Both analytical and numerical results show that it is feasible to use helium as a surface probe.

* While this work was in progress and the treatment of the surface potential was mostly completed a paper appeared in the literature using the same general approach. See reference 23.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgement</td>
<td>1</td>
</tr>
<tr>
<td>Summary</td>
<td>2</td>
</tr>
<tr>
<td>List of Symbols</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>2. GAS-SURFACE POTENTIAL</td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>2</td>
</tr>
<tr>
<td>2.2 Fourier Analysis</td>
<td>2</td>
</tr>
<tr>
<td>2.3 Thermal Average</td>
<td>5</td>
</tr>
<tr>
<td>2.4 The Morse Potential</td>
<td>6</td>
</tr>
<tr>
<td>2.5 Smooth Potential Approximation for Metals</td>
<td>9</td>
</tr>
<tr>
<td>3. SURFACE SCATTERING AND TRANSITION PROBABILITIES</td>
<td></td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>9</td>
</tr>
<tr>
<td>3.2 Hard-Cube Model</td>
<td>11</td>
</tr>
<tr>
<td>3.2.1 The Hard-Cube Potential</td>
<td>11</td>
</tr>
<tr>
<td>3.2.2 The Impulse Approximation</td>
<td>11</td>
</tr>
<tr>
<td>3.2.3 Thermal Average Over the Boltzmann Factor</td>
<td>15</td>
</tr>
<tr>
<td>3.2.4 Transition Probability</td>
<td>17</td>
</tr>
<tr>
<td>3.3 Soft-Cube Model</td>
<td>17</td>
</tr>
<tr>
<td>3.3.1 Distorted Wave Solution</td>
<td>17</td>
</tr>
<tr>
<td>3.3.2 Thermal Average Over the Boltzmann Factor</td>
<td>19</td>
</tr>
<tr>
<td>3.3.3 Linear Term Analysis</td>
<td>21</td>
</tr>
<tr>
<td>4. NUMERICAL RESULTS AND CONCLUSIONS</td>
<td></td>
</tr>
<tr>
<td>4.1 Comparison of the Multiple Phonon Analysis to the Linear Analysis</td>
<td>22</td>
</tr>
<tr>
<td>4.2 Hard-Cube Results</td>
<td>23</td>
</tr>
<tr>
<td>4.3 Soft-Cube Results</td>
<td>23</td>
</tr>
<tr>
<td>4.4 General Conclusions</td>
<td>24</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>25</td>
</tr>
</tbody>
</table>
### SYMBOLS

The following list contains most of the symbols used in the present work. Some symbols have two meanings that should be clear from the context in which they are used.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Parameter in the Morse function</td>
</tr>
<tr>
<td>b, b₁</td>
<td>Lattice spacing</td>
</tr>
<tr>
<td>B</td>
<td>Parameter for wave function defined in Appendix A</td>
</tr>
<tr>
<td>Bₙₘ</td>
<td>Special function defined in equation (3.25)</td>
</tr>
<tr>
<td>c</td>
<td>Parameter in exponential potential</td>
</tr>
<tr>
<td>D</td>
<td>Parameter in the Morse function</td>
</tr>
<tr>
<td>E</td>
<td>Energy of the incident particle</td>
</tr>
<tr>
<td>F₀(z)</td>
<td>Fourier coefficient</td>
</tr>
<tr>
<td>g(ν,λ,z)</td>
<td>Special function defined in equation (2.28)</td>
</tr>
<tr>
<td>gᵣₙ(K)</td>
<td>Fourier transform of the oscillator wave function</td>
</tr>
<tr>
<td>ℎ</td>
<td>Planck constant divided by 2π</td>
</tr>
<tr>
<td>Hₙ(x)</td>
<td>Hermite polynomial</td>
</tr>
<tr>
<td>i</td>
<td>Integer and √-1</td>
</tr>
<tr>
<td>J</td>
<td>Modified Bessel function</td>
</tr>
<tr>
<td>1</td>
<td>Integer</td>
</tr>
<tr>
<td>k</td>
<td>Integer, wave number</td>
</tr>
<tr>
<td>kₘ</td>
<td>Initial wave number</td>
</tr>
<tr>
<td>kₙ</td>
<td>Final wave number</td>
</tr>
<tr>
<td>Kᵣₙ</td>
<td>Modified Bessel function</td>
</tr>
<tr>
<td>K₀</td>
<td>Fourier transform vector</td>
</tr>
<tr>
<td>ℓ</td>
<td>Reciprocal lattice vector</td>
</tr>
<tr>
<td>ℓ₀</td>
<td>Magnitude of ℓ₀</td>
</tr>
<tr>
<td>L₀ₙ</td>
<td>Laguerre polynomial</td>
</tr>
<tr>
<td>m</td>
<td>Mass of the gas particle, integer denoting the initial state</td>
</tr>
</tbody>
</table>
\( M \)  
Integer denoting number of atomic sites, mass of solid atom

\( n \)  
Integer denoting the final state

\( N \)  
Number of atoms in the surface plane

\( P_{nm} \)  
Probability of transition from \( m \) to \( n \)

\( \vec{r} \)  
Position vector

\( \vec{r}_n \)  
Position vector of the \( n^{th} \) nucleus

\( r_0 \)  
Parameter in the Morse function

\( R \)  
Change of variable defined in equation (3.9)

\( q, q_m, q_n \)  
Modified wave number for the exponential wave function defined in Appendix A

\( T \)  
\( T_s \)  
\( u, u_\perp \)  
\( u_n \)  
\( u_{ll} \)  
\( V(\vec{r}) \)  
\( V_0 \)  
\( V_{osc} \)  
\( x \)  
\( x_n \)  
\( y \)  
\( z \)  
\( \alpha \)  
\( \beta \)  
\( \Gamma(z) \)  
\( \delta \)  
Greek Symbols

\( \alpha \)  
Integer in Laguerre polynomial, area of unit cell in the lattice

\( \beta \)  
Parameter in equation (2.23)

\( \Gamma(z) \)  
Gamma function

\( \delta \)  
Parameter defined in equation (3.52)
\( \delta(x) \)  
\( \delta_{nm} \)  
\( \theta \)  
\( \mu \)  
\( \xi \)  
\( \rho \)  
\( \sigma \)  
\( \phi \)  
\( \phi_n \)  
\( \chi_k \)  
\( \psi_n \)  
\( \omega \)  

Dirac delta function  
Kronecker delta function  
Einstein temperature of the solid  
Mass ratio \((m/M)\)  
Parameter for equation (2.28)  
Variable defined by equation (3.10)  
Parameter defined by equations (3.22), (3.23) and (3.28)  
Phase shift in wave function in Appendix A  
Plane wave function  
Wave function  
Oscillator wave function  
Angular frequency of oscillator
1. INTRODUCTION

In recent years there has been a growing interest in the investigation of gas-surface interactions. This growth has brought about such vast improvements in technology that it is currently possible to scatter gas particles from carefully defined surfaces and measure reflected velocity and flux distributions with a fair amount of certainty in the results. Being able to accurately measure details of the scattering process opens the possibility of using gas particles to measure surface properties of solids. This is of special interest because all other scattering particles such as neutrons, electrons and X-rays reveal information about the bulk but usually little about the surface. Low energy electrons have been used to investigate surface properties but at best this method involves several atomic layers. Gas atoms on the other hand scatter directly from the surface, (except of course for high energy particles that may penetrate into the solid). Thus it seems that a lighter gas like helium could possibly be used as a surface probe to determine surface properties such as the phonon dispersion.

To obtain the phonon dispersion from the scattering data it is a great advantage to show that most of the inelastic scattering comes from one phonon transitions and all higher transitions can be neglected. An analogous situation occurred with the scattering of neutrons from the solid bulk. In 1944 Weinstock (1) was able to show that under certain conditions higher order phonon transitions could be neglected. This property established neutrons as a valuable tool for determining the bulk phonon dispersion relations. If the one phonon assumption could be justified for gas particles scattering from the surface, the gas would be a surface probe just as neutrons have been for the bulk. It is our main purpose here to do some calculations investigating the number of phonon transitions based on two simple potential models: the hard-cube and the soft-cube.

For any scattering event the interaction potential plays the central role in determining the outcome of the event. Unfortunately the potential between the gas and the solid is not known at the present time. There are several models in the literature each being tailored for a specific situation e.g., either high or a low incident energy. In the thermal energy range two of the most successful models have been the so called hard-cube model developed by Logan and Stickney (2) and the soft-cube model developed by Logan and Keck (3). Both models are one dimensional potentials with the scattered flux being a result of inelastic collisions with the surface atom in thermal motion. In both developments the collision and the surface atom motion was treated using classical mechanics. These two potential models will be the potentials used in the present calculations but both the collision and the surface atom motion will be treated quantum mechanically.

Before doing these calculations we will first investigate the basis for assuming a one dimensional potential of interaction. To do this a Fourier analysis will be used. This analysis will show that the interaction potential can be conveniently represented by a two dimensional Fourier series with the coefficient depending upon the distance from the surface. This approach shows very clearly the foundations and limits on assuming a one dimensional model. In addition it provides a convenient way of describing the surface and illustrates other properties of the surface. With this as a foundation we will proceed with the phonon transition probability calculations.
2. GAS-SURFACE POTENTIAL

2.1 Introduction

There are several (4,5,6) detailed discussions on the interaction potential with abundant references available in the literature so there is no need for a detailed discussion here. We will however point out a few of the basic assumptions involved in the present development. First the surface is considered to be perfectly clean. This means a complete absence of absorbed gases. Second the surface is assumed to be structurally perfect i.e., no macroscopic or atomic imperfections. Third because we are mainly interested in helium for the gas species, the development will be directed toward physisorption. These assumptions are all straightforward and until more knowledge is gained about the surface, they are necessary.

It will also be assumed that the potential can be modelled by a sum of pairwise potentials. This assumption is not necessary in the sense that other models could be chosen. However the pairwise model has enjoyed wide use although not always with great success (7). It is appealing mathematically because it provides a convenient way of constructing a periodic potential. For this reason it will be used in the following development but we also point out that the basic concept of using a Fourier analysis is general and does not depend on the pairwise assumption.

2.2 Fourier Analysis

We represent the crystal by a Bravis lattice restricted to the half space \( z < 0 \) where we choose the x-y plane parallel to the crystal surface and the z coordinate perpendicular to this plane. Each nucleus in the crystal has a thermal motion centered about some equilibrium point. This equilibrium point is associated with a point in the Bravis lattice. To construct a mathematical model of the potential between the crystal and a particle exterior to the crystal we imagine that there exists a potential between each lattice point and the particle. The total potential is the sum of these pairwise potentials and is written

\[
V(\mathbf{r}) = \sum_n V(\mathbf{r} - \mathbf{r}_n)
\]  

(2.1)

where \( n \) runs over the whole crystal. The vector, \( \mathbf{r}_n \), represents the position of the \( n^{th} \) nucleus and can be written as

\[
\mathbf{r}_n = \mathbf{x}_n + \mathbf{\tilde{u}}_n
\]  

(2.2)

where \( \mathbf{x}_n \) is the equilibrium position (at a lattice point) of the \( n^{th} \) nucleus and \( \mathbf{\tilde{u}}_n \) is the thermal displacement of the \( n^{th} \) nucleus.

Next we introduce the transform pair

\[
V(\mathbf{r}) = \int \frac{d\mathbf{K}}{(2\pi)^3} V(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}}
\]  

(2.3)

and
\[
\mathbf{v}(\mathbf{k}) = \int d\mathbf{r} \, \mathbf{v}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} \tag{2.4}
\]

Substituting equations (2.1) and (2.2) into equation (2.4) yields
\[
\mathbf{v}(\mathbf{k}) = \int d\mathbf{r} \sum_n \mathbf{v}(\mathbf{r} - \mathbf{x}_n - \mathbf{u}_n) e^{-i\mathbf{k} \cdot \mathbf{r}} \tag{2.5}
\]

Because the limits of integration are infinite we can change variables
\[
\mathbf{r}' = \mathbf{r} - \mathbf{x}_n - \mathbf{u}_n \tag{2.6}
\]
to obtain
\[
\mathbf{v}(\mathbf{k}) = \left\{ \int d\mathbf{r}' \, \mathbf{v}(\mathbf{r}') e^{-i\mathbf{k} \cdot \mathbf{r}'} \right\} \sum_n e^{-i\mathbf{k} \cdot (\mathbf{x}_n + \mathbf{u}_n)} \tag{2.7}
\]

Next we split the sum on \( n \) into three sums each one extending over one coordinate in \( x-y-z \) space. We choose the \( i \) integer to be in the \( z \) direction. In doing this it must be remembered that in general both the equilibrium position and the thermal motion will be different for each layer near the surface. That is, we would expect the thermal displacement of the nuclei near the surface to be larger than that in the bulk (see Reference 8) and there is the possibility that the lattice spacing is different near the surface. To accommodate this we will put an extra subscript, \( i \) on the displacement vectors. With this we write
\[
\mathbf{v}(\mathbf{k}) = \left\{ \int d\mathbf{r}' \, \mathbf{v}(\mathbf{r}') e^{-i\mathbf{k} \cdot \mathbf{r}'} \right\} \sum_i e^{-i\mathbf{u}_i \mathbf{k}_i} e^{-i\mathbf{z}_i \mathbf{k}_i} \left\{ \sum_j e^{-i\mathbf{y}_j \mathbf{k}_j} \right\} x \sum_k e^{-i\mathbf{x}_k \mathbf{k}_i} \tag{2.8}
\]

The three integer sums are the so-called structure factors. Because we are interested in the value of the potential near the surface, care must be exercised in their evaluation. The last two are the same as the usual structure factors in the bulk except for the extra subscript \( i \). If we consider that the effect of \( i \) is constant throughout each layer, then the last two structure factors can be considered layer by layer and evaluated in the usual manner. We write
\[
\sum_j e^{-i\mathbf{y}_j \mathbf{k}_j} = \sum_M e^{-i\mathbf{y}_j \mathbf{b}_i} \tag{2.9}
\]

where \( b_i \) is the lattice spacing in the \( y \) direction in the \( i \)th layer and \( 2M+1 \) is the number of lattice points in the \( y \) direction. Statement (2.9) can be easily shown to be
\[
= \frac{1 - e^{-i\mathbf{y}_1 \mathbf{b}_i}}{1 - e^{-i\mathbf{y}_1 \mathbf{b}_i}} + \frac{1 - e^{-i\mathbf{y}_M \mathbf{b}_i}}{1 - e^{-i\mathbf{y}_M \mathbf{b}_i}} - 1. \tag{2.10}
\]

Since we are considering an infinite lattice in the \( x-y \) directions, the number \( M \)
is very large. This being the case the first two terms in equation (2.10) oscillate very rapidly with small variations in $K_y$ so any averaging process will have a null result unless both the numerator and the denominator are zero. This means that $K_y$ must be an integral multiple of $2\pi/b$, which is exactly the condition for a reciprocal lattice vector. Under this condition equation (2.9) is of the order $2M+1$. The sum on $k$ is evaluated in exactly the same way. The product of these two terms is of the order of the number of unit cells in the $i$th layer which we will call $N$.

The sums on $j$ and $k$ effectively act like delta functions so that the only allowed values of $K_y$ and $K_x$ are those coinciding with the reciprocal lattice vector space. This simply means that the continuous Fourier transform is converted to a discrete sum. To complete this conversion it is convenient to adopt the normalization.

$$N = \frac{(2\pi)^2}{\alpha_i} \tag{2.11}$$

where $\alpha_i$ is the area of a unit cell on the $i$th layer. Rewriting equation (2.7) we have

$$\vec{V}(\vec{K}') = \frac{(2\pi)^2}{\alpha_i} \sum \frac{e^{-i\vec{u}_{i1,1} \cdot \vec{r}_i}}{K_y} e^{-iK_yz_i} \int d\vec{r}' \, \vec{V}(\vec{r}') e^{-i\vec{K}' \cdot \vec{r}'} \tag{2.12}$$

where $\vec{u}_{i1}$ is the two dimensional reciprocal lattice vector in the $i$th plane and $K' = (\vec{L}_i, K_y)$. We use the prime to remind ourselves that $\vec{F}$ is now discrete in the parallel directions but still continuous in the perpendicular direction.

The sum on $i$ in equation (2.12) cannot be evaluated like the other two structure factors because in the neighbourhood of the surface the finite extent of the crystal must be taken into account. This is our first deviation from the usual three dimensional development and it is here that the surface is expressed mathematically. Because of this the $i$ structure factor must be retained in its present form and the Fourier transform in the perpendicular direction remains continuous.

The potential can now be written

$$V(\vec{r}, \vec{u}) = \sum_i \sum_{\vec{L}_i} \frac{e^{i\vec{L}_i \cdot \vec{r}}}{\alpha_i} \tag{2.13}$$

where

$$\frac{e^{i\vec{L}_i \cdot \vec{r}}}{\alpha_i} = \int \frac{dK_y}{2\pi} \, V(\vec{L}_i, K_y). \tag{2.14}$$

Equation (2.13) is the general result of interest. It shows that the potential outside of the crystal can be viewed as a two dimensional discrete Fourier transform with the coefficients depending on the distance from the surface and the temperature (i.e., $\vec{u}_i$) of the crystal. In a later section by a specific example the properties of the Fourier coefficients will be illustrated.
2.3 Thermal Average

For elastic scattering or for plotting the potential function it is useful to approximate it by its thermal average. Symbolically this can be written

\[ V(r, u) = \sum_i < F_{k_i} (z, \hat{u}_i) >_T e^{i \hat{r} \cdot \hat{u}_i} \] (2.15)

where

\[ < F_{k_i} >_T = \int \frac{dK}{2\pi} < V(K') >_T. \] (2.16)

Substituting this in equation (2.12) we find

\[ \langle V(K') \rangle_T = (2\pi)^2 \sum_i e^{i k_z z_i} dK \cdot \hat{u}_i e^{i K' \cdot r} \] (2.17)

Ott (9) showed that

\[ \langle e \rangle_T = e^{-\sum_i \alpha_i (1/2) \langle (K' \cdot \hat{u}_i)^2 \rangle_T} \] (2.18)

which is usually written as \( e^{-\sum_i \alpha_i} \) and is the Debye-Waller factor for the \( i \)th layer. The explicit evaluation of this factor is difficult and for general crystals it is impossible to evaluate analytically (see Reference 10). In our present problem this is further complicated by the fact that the thermal motion is more complex near the surface. Since our interest in this section is mostly qualitative, we will avoid these difficulties by two assumptions. These assumptions greatly simplify the analysis but still illustrate the basic points. First we will assume that the properties at the surface are the same as those for the bulk. This allows us to drop the subscript \( i \) from all the parameters except \( z_i \). This assumption could be reasonable for ionic crystals because of the long-range forces. Second we will consider only a cubic crystal.

With these restrictions equation (2.18) becomes

\[ \langle (1/2) \langle (K' \cdot \hat{u})^2 \rangle_T \rangle_T = \langle u^2 \rangle e^{-\sum_i \alpha_i (1/2) \langle (k_{z_i}^2 / 2) \rangle_T} \] (2.19)

Substituting this into equation (2.17) we have

\[ < V(K') >_T = \frac{(2\pi)^2}{\alpha} \left\{ \sum_i e^{-i k_{z} z_i} \right\} e^{-\sum_i \alpha_i (1/2) \langle k_{z_i}^2 / 2 \rangle_T} \langle u^2 \rangle \int d\hat{r} V(\hat{r}) e^{i K' \cdot \hat{r}}. \] (2.20)

The last factor is the three dimensional Fourier transform of the pairwise potential. The two middle factors are the Debye-Waller factors and the first factor is the structure factor.
2.4 The Morse Potential

Up to this point the analysis has been valid for any pairwise potential provided its Fourier transform exists. We now wish to choose a specific potential function to illustrate the behaviour of the Fourier coefficients. A particularly convenient function is the Morse function because it has a general form that a realistic potential must have and its Fourier transform exists. The Morse function is

\[ V(r) = D \left\{ \frac{-2(r-r_0)}{a} \right\} \left\{ \frac{r-r_0}{a} \right\} \]

and has for its Fourier transform

\[ \int dr V(r) e^{-ik' r} = \frac{16\pi D r_0}{a} \left\{ \frac{r_0}{a} \right\} \left\{ \frac{1}{[\beta^2 + K_{\perp}^2 + K_{\parallel}^2]^2} \right\} \]

For the resulting potential it is only necessary to substitute this result into equation (2.20) or equation (2.13) depending upon which form is desired. Then the integration on \( K_{\perp} \) and the sum on \( i \) must be completed. For the Morse function the integration on \( K_{\perp} \) is straightforward and involves the integral

\[ \int dK_{\perp} \frac{e^{iK_{\perp}(z-z_i)}}{[\beta^2 + K_{\perp}^2]^2} = 2 \int_0^{\infty} dK_{\perp} \frac{\cos[K_{\perp}(z-z_i)]}{[\beta^2 + K_{\perp}^2]^2} e^{-K_{\perp}^2} < u^2>/2 \]

where \( \beta^2 = (2/a)^2 + \ell^2 \) or \((1/a)^2 + \ell^2\). Integral (2.23) is a standard cosine transform and results in

\[ = \frac{\pi}{4} \frac{1}{\beta^3} \left\{ \frac{1-<u^2>\beta^2 + (z-z_i)\beta}{2} \right\} e^{-\beta(z-z_i)} \text{Erfc}\left[\beta \frac{<u^2>}{2} + \frac{(z-z_i)}{\sqrt{2<u^2>}}\right] \]

\[ + \left[ 1-<u^2> \beta^2 - (z-z_i)\beta \right] e^{-\beta(z-z_i)} \text{Erfc}\left[\beta \frac{<u^2>}{2} + \frac{(z-z_i)}{\sqrt{2<u^2>}}\right] \]

A significant simplification can be made by remembering that \( <u^2> \) is a small number, say much less than \( 1^{\circ}A \) and restricting our interest to the region outside of the crystal i.e., \( z > 0 \). This restriction is not serious because the turning point (or penetration depth) is in this region. That is we are saying that because of the finite size effect of the atoms the smallest values for \( z \) of physical interest

\* \( ^{\circ}A \) is the Angstrom unit
are those for $z > 0$. Using these we have the condition

$$\frac{z - z_1}{\sqrt{\langle u^2 \rangle}} \gg 1 .$$ \hspace{1cm} (2.25)

Using this condition we can write approximately

$$\text{Erfc} \left[ \frac{\sqrt{\langle u^2 \rangle}}{2} \beta + \frac{(z-z_1)}{\sqrt{2\langle u^2 \rangle}} \right] = \begin{cases} 2 & \text{for } - \\ 0 & \text{for } + . \end{cases}$$ \hspace{1cm} (2.26)

And with the same condition the last term in equation (2.24) can be neglected. This results in the much simpler form for equation (2.24)

$$= \frac{\pi}{2} \frac{1}{\beta^3} \left[ 1 - \frac{\langle u^2 \rangle}{\beta^2} + \frac{(z-z_1)}{\beta} \right] e^{\beta^2 \langle u^2 \rangle} e^{-\beta(z-z_1)}.$$ \hspace{1cm} (2.27)

The most interesting thing about this function is that it is proportional to \( \frac{\langle u^2 \rangle}{2} \). When this function is substituted in Equation (2.20) and finally into equation (2.14), this factor cancels out. This means that the Debye-Waller factor will not appear in the final potential in its usual form. This is a direct consequence of assuming that the thermal motion in the normal direction is the same as in the parallel directions. This is not exact so the cancellation is not complete. However the Debye-Waller factor would involve the difference of the thermal motion in these two directions and the effect of the thermal motion for elastic scattering would therefore be less than one might expect.

Before substituting equation (2.27) in the final form it is convenient to introduce the notation

$$g(\xi, \lambda, z_1) = \left[ 1 - \frac{\langle u^2 \rangle}{\beta^2} + \frac{\xi}{a} \right] \beta^2 \frac{\langle u^2 \rangle}{2} + \frac{\xi}{a} \beta \frac{(z-z_1)}{\beta}.$$ \hspace{1cm} (2.28)

where \( \xi = 1 \) or 4 depending on which term in the Morse function it corresponds to. With this notation the final potential is

$$<V(\mathbf{r})>_T = \frac{4\pi D \alpha}{a^3} \sum_{l} \sum_{i} \left\{ e^{i \mathbf{l} \cdot \mathbf{r}_{1i}} g(4, \lambda, z_1) - g(1, \lambda, z_1) \right\} e^{-\frac{\xi}{a^2} \frac{\langle u^2 \rangle}{\beta^2} + \frac{\xi}{a} \beta \frac{(z-z_1)}{\beta}}.$$ \hspace{1cm} (2.29)

We note that even though the Debye-Waller factor does not appear in its usual form, the Fourier coefficients are still functions of the temperature through \( \langle u^2 \rangle \). However equation (2.28) indicates that the temperature effect on the elastic peaks should be fairly weak.
Next we consider the sum on $i$. For the simple cubic case this sum is easily carried out analytically. Here we consider a crystal orientation so that a plane in the edge of the cube is exposed to the surface. The parameter $z_i$ is equal to $-ib$ where $b$ is the distance between planes and $i$ an integer runs from zero to infinity. Then the two types of sums appearing in equations (2.29) are evaluated as follows:

$$\sum_{i=0}^{\infty} e^{-ib\sqrt{b^2 + \xi/a^2}} = \frac{1}{1-e^{-b\sqrt{b^2 + \xi/a^2}}} \quad (2.30)$$

and

$$\sum_{i=0}^{\infty} i e^{-ib\sqrt{b^2 + \xi/a^2}} = e^{-b\sqrt{b^2 + \xi/a^2}} \quad (2.31)$$

Using these two relations we can write

$$\sum_{i} g(\xi, \ell, z_i) = e^{\frac{z\sqrt{b^2 + \xi/a^2}}{2a^2}} \quad (2.32)$$

And for the final form for the thermally averaged potential we have

$$\langle V(\mathbf{r}) \rangle_T = \frac{4\pi De}{Ca} \sum_{\ell} \left\{ e^{i\mathbf{k} \cdot \mathbf{r}} \{g(4, \ell, 1) - g(1, \ell)\} \right\} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (2.33)$$

which can be written

$$\langle V(\mathbf{r}) \rangle_T = \sum_{\mathbf{k}} F_\ell(z) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (2.34)$$

This is the form for the potential that we set out to obtain. It is simply a two dimensional Fourier transform with its coefficients being a function of the distance from the origin of the first layer. How the coefficients vary as a function of $\ell$ for a fixed distance is a result of how "rough" the potential is in the $x$-$y$ plane. For example if the first coefficient is the only significant coefficient, the potential is very smooth. If many coefficients are involved, then the potential is very "rough" or has a significant variation in the $x$-$y$ plane. For example the hard sphere model such as the one used by D. P. Jackson (11) would involve many terms in the Fourier expansion for the repulsive part.
but one term for the smooth attractive part.

A particularly interesting feature of equation (2.34) is that the number of significant coefficients depend upon the distance from the surface. By investigating equation (2.32) it is apparent that the coefficients for higher \( l \)'s drop off much faster for larger \( z \)'s than for smaller \( z \)'s. This means that the potential gets smoother as one goes away from the crystal and gets "rougher" going closer. A low energy particle may very well be turned around before it gets into the rough region of the potential and therefore scatter mainly from a smooth potential whereas a high energy particle would penetrate farther and would be more affected by the \( x-y \) roughness. This is probably why smooth potentials seem to give reasonable results for thermal energies but for high energies (i.e., satellite velocities) one has to go to three dimensional models. This is also supported by Oman's (12) discussion of thermal and structure scattering.

2.5 Smooth Potential Approximation for Metals

Despite careful efforts experimenters (13) have not been able to observe diffraction for gas-metal systems. This implies that for thermal energy beams the surfaces of metals (for helium) appear to be smooth. In equation (2.34) this would mean that

\[
F_o(z) \gg F_{l 
eq 0}(z)
\]  

(2.35)

for the \( z \) values in the scattering region. It is this inequality that forms the basis for assuming a one dimensional model for the interaction potential. In particular this inequality clearly shows the assumptions made in choosing the hard or soft cube models. The difference between the two models is in the choice of the form for \( F_0 \). The hard-cube assumes the form

\[
F_0(z) = \begin{cases} 
F_0 \to \infty & z \leq 0 \\
0 & z > 0 
\end{cases}
\]  

(2.36)

and the soft-cube assumes

\[
F_0(z) = V_0 \ e^{-z/c}
\]  

(2.37)

where \( V_0 \) and \( c \) are constants. It is these two potentials that will concern us in the next section.

One additional point must be made about using the potential form in equation (2.34) for scattering from metals. This equation was derived as the thermally averaged potential and thus can only describe elastic scattering. To calculate the inelastic scattering one must return to the potential form before the thermal average is taken. In doing this one finds that the argument of \( F \) must have \( z \) replaced by \( z-u \) where \( u \) is the thermal motion normal to the surface. The parallel motion does not enter into this one dimensional form.

3. SURFACE SCATTERING AND TRANSITION PROBABILITIES

3.1 Introduction

In the last section we showed that for low penetration depths it seems reasonable to assume a potential of the form \( F_0(z-u) \). To completely determine
the Hamiltonian of the gas-solid system the operators for the gas and the solid are needed as well as \( F(z-u) \). Because we are concerned only with the inert gases and helium in particular there is no rotational or vibrational modes for the gas. The lowest electronic transition requires more energy than those energies concerned so the electronic states can be neglected. For these reasons the gas can be accurately modelled by a particle with a mass equal to the gas mass. Its operator is simply the kinetic operator.

The solid is much more complicated and a normal mode analysis should be used as was done for example by Jackson and Howarth (14). However unless the one phonon assumption is invoked immediately the problem becomes unwieldy. Since we are interested in comparing the probabilities for different phonon transitions, this assumption is impossible. In fact it is this assumption that we would like to verify. To get around this problem we restrict the surface atom to one frequency of oscillation as in Einstein's theory of the specific heat of solids. Furthermore we will consider the surface atom to be bound harmonically to an immovable solid surface. This is exactly the same as in the original soft-cube model except we treat it quantum mechanically. With these simplifications the Schrödinger equation becomes

\[
- \frac{\hbar^2}{2m} \frac{\partial^2 \chi}{\partial z^2} (z,u) - \frac{\hbar^2}{2M} \frac{\partial^2 \chi}{\partial u^2} (z,u) + [V_{\text{osc}} + F(z-u)] \chi(z,u) = E \chi(z,u) \quad (3.1)
\]

There are three basic reasons why this equation is difficult to solve. First it is a nonseparable equation in two variables. If it were separable, it would be much easier to solve. This line of reasoning leads to ways of getting approximate solutions. Later we will take full advantage of this.

The second complication is due to the existence of a potential well. This creates the possibility of a collision complex (see Reference 15). For general gas-solid systems this is important and leads to adsorption and line broadening. However in the next section we will be dealing only with helium. The energy well for helium on most solids is very small. For example helium-tungsten has an energy about .002 electron volts which is more than an order of magnitude below the gas energies that we will be considering. For this reason one would expect the effect of collision complexes would be small for helium and we will neglect it. This means the potential well will only classically accelerate and decelerate the particle.

We might also point out that if the collision complex becomes important, quite likely the one dimensional assumption will become poor. This is because as the gas becomes adsorbed, even for short times, its probability of interacting strongly in the x-y directions will be increased greatly.

The third reason is that equation \((3.1)\) describes a direct or head-on collision. This involves large changes of momentum in the normal direction and convenient approximations like the first Born approximation cannot be used. There are however other approximations that can be considered and this will be done in the next section.
3.2 Hard-Cube Model

3.2.1 The Hard-Cube Potential

The general form for the hard-cube potential was given by equation (2.36). However, it is more convenient (but not necessary) to start with the exponential form given by equation (2.37) and then take the limits \( V_o \to \infty \) and \( c \to 0 \). The starting potential is then

\[
F_0 = V_o e^{-c(z-u)}
\]

and the limits will be taken later during the calculations.

3.2.2 The Impulse Approximation

The impulse approximation is useful in problems where the collision time is short compared to some characteristic time. The collision time is estimated by the time of collision or the time spent by the scattered particle in the vicinity of the target. For the hard-cube model the actual collision time is zero so it is more meaningful to use an estimate for the time the gas spends in the region occupied by the harmonic oscillator. We estimate this by dividing the oscillator displacement by the free particle velocity. The characteristic time is taken to be the time for one oscillation in the ground state. From this the criterion for the impulse approximation is

\[
\frac{\sqrt{\frac{\mu}{2}} \text{cutoff} \omega}{E} \ll 1
\]

where \( \mu \) is the mass ratio, \( \omega \) is the ground state angular frequency, and \( E \) is the incident gas energy (normal to surface). By assuming \( E \) to be about 2kT at room temperature for helium on gold and estimating \( \omega \) from the Debye cutoff the factor in expression (3.3) is about .05.

We now wish to apply this approximation in calculating the phonon transition probabilities. The central problem is the calculation of a quantity called the T-matrix from which the probabilities can be found. The following calculation of this quantity using the impulse approximation follows the development given in reference 15.

The exact T-matrix is given by

\[
T = \int \int e^{-izk_n} \Psi_n^*(u) \frac{V_o}{\sqrt{2\pi}} \int e^{-iKu} \Psi_n(u) dzdu
\]

where we use the convention that \( k_n \), the final state wave vector, is the absolute value with the minus sign put in the exponential. There should be an energy conserving delta function in equation (3.4). However if we remember that the total energy must be conserved there is no loss in its omission. The function \( \Psi \) is the wave function for the oscillator and \( \chi(z,u) \) is the solution to equation (3.1).

To manipulate this T-matrix a form suitable for the impulse approximation we introduce the transform pair

\[
g_n(K) = \frac{1}{\sqrt{2\pi}} \int e^{-iKu} \Psi_n(u) du
\]
and
\[ \psi_n(u) = \frac{1}{\sqrt{2\pi}} \int e^{iku} g_n(K) dK. \]  
(3.6)

Next we temporarily introduce the first Born approximation
\[ \chi_b(z,u) \sim e^{-ik} \psi_m(u) \]  
(3.7)

where the subscript m is the initial state of the oscillator. The final result will not depend upon the Born approximation. Substituting equations (3.5), (3.6), and (3.7) into equation (3.4) we find
\[ T^b = \frac{1}{2\pi} \int \int \int e^{-i(k+k')} \delta(K-K') \]  
\[ \cdot e^{iu(K_m-K_n)} F_0(z-u) g_n^*(K_n) g_m(K_m) dK dK' dz du \]  
(3.8)

where the superscript b reminds us that this T-matrix is in the first Born approximation. We now make a change of variable according to
\[ R = \frac{mz + Mu}{m+M} = \frac{\mu z + u}{1+\mu} \]  
(3.9)

and
\[ \rho = z - u \]  
(3.10)

where
\[ \mu = \frac{m}{M}. \]  
(3.11)

The parameter m is the gas mass and M is the solid atom mass. No confusion should arise in the double use of m because the context makes the meaning clear. Using this change of variable equation (3.8) becomes
\[ T^b = -\frac{1}{2\pi} \int \int \int e^{ik'(K_n - K_m + K_m)} \]  
\[ \cdot g_n^*(K_n) g_m(K_m) dK dK' dR dp \]  
\[ = -\int \int \delta(K_n - K_m + K_m) \]  
\[ \cdot e^{i\rho(K_n - K_m + \mu K_m)} F_0(\rho). \]  
(3.12)

where the delta function insures conservation of momentum.

The impulse approximation is introduced by noting that the integral over \( \rho \) is exactly the same as the integral evaluated in calculating the T-matrix for two body scattering in the first Born approximation. The impulse approximation is made by replacing this integral by the exact two body integral i.e., the first Born wave function
\[ \text{EXP} \left[ \frac{i\rho}{1+\mu} (-k_m - \mu K_m) \right] \]
is replaced by the exact two body wave function which we will call \( \chi^\prime \). The wave vector \( k' \) is defined by

\[
k' = \frac{k_{m} + \mu K_{m}}{1 + \mu}.
\]

This wave function is derived in Appendix A for an exponentially repulsive potential. We substitute this wave function into equation (3.13) and at the same time perform the integration on \( \rho \) to find

\[
T^\prime = \frac{\mu n^2}{2\pi mc} \int \frac{\Gamma(1 + iq_{m}')\sinh(\pi q_{m}')}{2ci(k_{m}' - \mu K_{m})/(1 + \mu)} \Gamma\left(\frac{\delta + iq_{m}'}{2}\right) \Gamma\left(\frac{\delta - iq_{m}'}{2}\right)
\]

\[
\times 5(-k_{m} - k_{n} - K_{m} + K_{n})g_{n}^{*}(K_{n})g_{m}(K_{n})dK_{n}dK_{m}
\]

where

\[
\delta = 2 \left[ \frac{i(k_{m} - \mu K_{n})c}{1 + \mu} + 1 \right]
\]

and the other variables are defined in Appendix A. The T-matrix now no longer depends on a weak interaction i.e., the first Born approximation. The only restriction is that the collision time must be short.

One integration in equation (3.15) is trivial because of the Dirac delta function. However the other integral is quite involved so it is a convenient time to perform the limits. We take the limits \( c \to 0 \) and \( V_{0} \to \infty \) but in such a manner that the product \( cB \) remains a constant. We then have the limits

\[
\text{Limit } \delta \to 2
\]

\( c \to 0 \)

\( q_{m}' \to 0 \)

\( V_{0} \to 0 \)

\( (cB) \)

\( \text{q}' \to 1 \)

Using these equation (3.15) reduces to

\[
\text{limit } T^\prime = \frac{\mu n^2}{2\pi c} \int k_{m}' g_{n}^{*}(K_{n} - k_{m} - k_{m}')g_{m}(K_{n})dK_{n}
\]

To complete this integral the function \( g(K) \) must be known explicitly. The wave function \( \Psi_{n}(u) \) is derived in any basic textbook on quantum mechanics e.g., see reference 16. It is

\[
\Psi_{n}(u) = \frac{2^{-n/2}}{\sqrt{n!}} \left( \frac{M_{0}}{\pi n^{2}} \right)^{1/4} \text{EXP} \left[ - \frac{M_{0}}{2} \right] H_{n} \left[ u \sqrt{\frac{M_{0}}{n}} \right]
\]

where \( H_{n} \) are Hermite polynomials. The function \( g(K) \) is easy found using equation (3.5) and is
\[ g_n(k) = \frac{2^{-n/2}}{\sqrt{\pi^n}} \left( \frac{\hbar}{m \omega} \right)^{1/4} (-i)^n \exp \left[ \frac{\hbar k^2}{2m \omega} \right] H_n \left[ \frac{\sqrt{\hbar k^2}}{\sqrt{m \omega}} \right] \] (3.20)

Substituting this into equation (3.18) yields

\[ T_{c \to 0} = \frac{\hbar^2}{2m} \frac{-n/2 - m/2}{\sqrt{\pi n! m!}} \left( \frac{\hbar}{m \omega} \right)^{1/2} \int \left( k + \mu k \right) e^{\frac{-\omega_n^2}{2}} e^{\frac{-\omega_m^2}{2}} \int H_n(\sigma_n) e^{\frac{-\sigma_n^2}{2}} H_m(\sigma_m) d\sigma_n d\sigma_m \] (3.21)

where

\[ \sigma_n = \sqrt{\frac{\hbar}{m \omega}} \left( k_n - k_m \right) \] (3.22)

and

\[ \sigma_m = \sqrt{\frac{\hbar}{m \omega}} k_m \] (3.23)

By using the recursion relation for Hermite polynomials equation (3.21) written

\[ T_{c \to 0} = \frac{\hbar^2}{2m} \frac{-n/2 - m/2}{\sqrt{\pi n! m!}} \left( \frac{\hbar}{m \omega} \right)^{1/2} \int \left( k + \mu k \right) e^{\frac{-\omega_n^2}{2}} e^{\frac{-\omega_m^2}{2}} \int H_n(\sigma_n) e^{\frac{-\sigma_n^2}{2}} H_m(\sigma_m) d\sigma_n d\sigma_m \] (3.24)

where

\[ B_{n,m} = \int e^{\frac{-\sigma_n^2}{2}} H_n(\sigma_n) e^{\frac{-\sigma_m^2}{2}} H_m(\sigma_m) d\sigma_n d\sigma_m \] (3.25)

With a change of variable this can be put in a standard form and evaluated yielding the results:

Case (i) \( m \geq n \)

\[ B_{n,m} = e^{-\sigma_n^2/4} \frac{2^m}{\sqrt{\pi n!}} \left( -\frac{\sigma_n^2}{2} \right)^{m-n} \frac{L_n}{L_n} \left( \sigma_n^2/2 \right) \] (3.26)

and

Case (ii) \( n \geq m \)

\[ B_{n,m} = e^{-\sigma_m^2/4} \frac{2^n}{\sqrt{\pi m!}} \left( -\frac{\sigma_m^2}{2} \right)^{n-m} \frac{L_m}{L_m} \left( \sigma_m^2/2 \right) \] (3.27)

where

\[ \sigma_n = \sqrt{\frac{\hbar}{m \omega}} \left( k_n + k_m \right) \] (3.28)

and the Laguerre polynomials, \( L_{n-m}^m \) are defined in Appendix B. To substitute equations (3.26) and (3.27) into equation (3.24) it is convenient to discuss three separate cases.

Case (i) \( n = m \) (elastic case)
For this case the T-matrix becomes

\[
T_{T \rightarrow 0} = \frac{ih^2}{2m} \left( -\frac{\sigma^2}{4} \right) e^\frac{\sqrt{\hbar \omega}}{\hbar} \left[ \frac{k^2}{2m} \left( -\frac{\sigma}{\sqrt{2}} \right)^{\alpha} L_n^\alpha \left( \frac{\sigma^2}{2} \right) - \frac{\mu}{\sqrt{\hbar \omega}} \right] L^\alpha \left( \frac{\sigma^2}{2} \right) \right] 
\]

Using the recursion relations given in Appendix B this can be put in the form

\[
T = \frac{ih^2}{2m} \left( -\frac{\sigma^2}{4} \right) e^\frac{\sqrt{\hbar \omega}}{\hbar} \left[ \frac{k^2}{2m} \left( -\frac{\sigma}{\sqrt{2}} \right)^{\alpha} L_n^\alpha \left( \frac{\sigma^2}{2} \right) - \frac{\mu}{\sqrt{\hbar \omega}} \right] L^\alpha \left( \frac{\sigma^2}{2} \right) \right] 
\]

Case (ii) m > n

Here T becomes

\[
T = \frac{ih^2}{2m} \left( -\frac{\sigma^2}{4} \right) e^\frac{\sqrt{\hbar \omega}}{\hbar} \left[ \frac{k^2}{2m} \left( -\frac{\sigma}{\sqrt{2}} \right)^{\alpha} L_n^\alpha \left( \frac{\sigma^2}{2} \right) - \frac{\mu}{\sqrt{\hbar \omega}} \right] L^\alpha \left( \frac{\sigma^2}{2} \right) \right] 
\]

where \( \alpha = m-n \). Then by the recursion relations we can write

\[
T = \frac{ih^2}{2m} \left( -\frac{\sigma^2}{4} \right) e^\frac{\sqrt{\hbar \omega}}{\hbar} \left[ \frac{k^2}{2m} \left( -\frac{\sigma}{\sqrt{2}} \right)^{\alpha} L_n^\alpha \left( \frac{\sigma^2}{2} \right) - \frac{\mu}{\sqrt{\hbar \omega}} \right] L^\alpha \left( \frac{\sigma^2}{2} \right) \right] 
\]

Case (iii) n > m

The recursion relations can be used here in an analogous fashion to write

\[
T = \frac{ih^2}{2m} \left( -\frac{\sigma^2}{4} \right) e^\frac{\sqrt{\hbar \omega}}{\hbar} \left[ \frac{k^2}{2m} \left( -\frac{\sigma}{\sqrt{2}} \right)^{\alpha} L_n^\alpha \left( \frac{\sigma^2}{2} \right) - \frac{\mu}{\sqrt{\hbar \omega}} \right] L^\alpha \left( \frac{\sigma^2}{2} \right) \right] 
\]

This completes the calculation of the T-matrix.

3.2.3 Thermal Average Over the Boltzmann Factor

The initial state of the surface oscillator has a statistical distribution of values which is a function of the solid temperature. To include this temperature one must average over the distribution. For the distribution function we take the Boltzmann distribution and calculate

\[
< |T|^2 > = \sum_m \left( 1 - e^{-n \hbar \omega / kT_s} \right)^{-mn \hbar \omega / kT_s} \left( |T|^2 e^{-n \hbar \omega / kT_s} \right) 
\]

Again this calculation is most easily done by considering three cases:
Case (i) \( n = m \)

This is the elastic case and both the gas particle and the oscillator retain the same energy. For this case we have

\[
|T|^{2} = (1-z) \left[ \frac{\hbar^{2}}{2m(1+\mu)} \right]^{2} \left[ k_{m} - \frac{\hbar \sigma}{\sqrt{M_{w} A}} \right]^{2} e^{-\sigma^{2}/2} \sum_{m=0}^{\infty} [I_{m}^{*}(\sigma^{2}/2)]^{2} z^{m} \tag{3.35}
\]

where \( z = e^{-\hbar W/2kT_{S}} \). The quantities factored out of the sum do not depend on the initial state of the oscillator. For example both \( k_{m} \) and \( \sigma \) depend on the initial state of the gas but not the oscillator.

Using the sum given in Appendix B the sum in equation (3.35) is easily evaluated yielding

\[
|T|^{2} = \left[ \frac{\hbar^{2}}{2m(1+\mu)} \right]^{2} \left[ k_{m} - \frac{\hbar \sigma}{\sqrt{M_{w} A}} \right]^{2} \exp \left[ -\frac{\sigma^{2}(1+z)}{2(1-z)} \right] I_{0} \left[ \frac{\sigma^{2} \sqrt{z}}{1-z} \right] \tag{3.36}
\]

where \( I_{N}(x) \) is a modified Bessel function as defined in reference 17 or 18.

Case (ii) \( m > n \)

This case describes the inelastic event where the final state of the oscillator is lower than the initial state i.e., the surface oscillator loses energy to the gas. To satisfy energy conservation the sum on \( m \) must run from \( m-n \) to infinity. The value \( m-n \) is the number of transitions and this restriction guarantees that the initial state will not be less than the number of transitions. For this to happen the oscillator would have to lose more energy than it possessed. With this condition we write

\[
|T|^{2} = (1-z) \left[ \frac{\hbar^{2}}{2m(1+\mu)} \right]^{2} \left[ k_{m} - \frac{\hbar \sigma}{\sqrt{M_{w} A}} \left( m-n + \frac{\sigma^{2}}{2} \right) \right]^{2} \left( \frac{\sigma^{2}}{2} \right)^{m-n} e^{-\sigma^{2}/2} x \sum_{m=m-n}^{\infty} z^{m} \frac{n!}{m!} \left[ L_{m-n}^{*} \left( \frac{\sigma^{2}}{2} \right) \right]^{2} \tag{3.37}
\]

By a change of integer this may be put into a form and evaluated by the sum in Appendix B. This yields

\[
|T|^{2} = \left[ \frac{\hbar^{2}}{2m(1+\mu)} \right]^{2} \left[ k_{m} - \frac{\hbar \sigma}{\sqrt{M_{w} A}} \left( m-n + \frac{\sigma^{2}}{2} \right) \right]^{2} z^{m-n/2} \exp \left[ -\frac{\sigma^{2}(1+z)}{2(1-z)} \right] x \sum_{m=m-n}^{\infty} I_{m-n} \left[ \frac{\sigma^{2} \sqrt{z}}{1-z} \right] \tag{3.38}
\]

Case (iii) \( n > m \)

In this case the oscillator gains energy from the gas particle. Since any initial state can gain energy, the sum in equation (3.34) starts at \( m = 0 \). It is evaluated as before and yields
\[ \langle |T|^2 \rangle = \left[ \frac{n^2}{2m(1+\mu)} \right]^2 \left[ k_m - \frac{\mu}{\sigma} \sqrt{\frac{\nu}{\kappa}} \left\{ m-n+ \frac{\sigma^2}{2} \right\} \right]^2 \frac{(m-n)/2}{Z} \exp \left[ -\frac{\sigma^2(1+z)}{2(1-z)} \right] \]

These three cases can be combined into one final form

\[ \langle |T|^2 \rangle = \left[ \frac{n^2}{2m(1+\mu)} \right]^2 \left[ k_m - \frac{\mu}{\sigma} \sqrt{\frac{\nu}{\kappa}} \left\{ m-n+ \frac{\sigma^2}{2} \right\} \right]^2 \frac{(m-n)/2}{Z} \exp \left[ -\frac{\sigma^2(1+z)}{2(1-z)} \right] \]

\[ \langle |T|^2 \rangle = \left[ \frac{n^2}{2m(1+\mu)} \right]^2 \left[ k_m - \frac{\mu}{\sigma} \sqrt{\frac{\nu}{\kappa}} \left\{ m-n+ \frac{\sigma^2}{2} \right\} \right]^2 \frac{(m-n)/2}{Z} \exp \left[ -\frac{\sigma^2(1+z)}{2(1-z)} \right] \]

**3.2.4 Transition Probability**

The probability for a given transition number is calculated from

\[ \langle |T|^2 \rangle \]

by dividing by the incoming flux and multiplying by the density of states. This is,

\[ P_{nm} = \left( \frac{m^2}{h^2} \right)^2 \frac{\langle |T|^2 \rangle}{k_m k_n} \]

In addition for ease of comparing the results we normalize \( P_{nm} \) such that the total number of transitions adds to 100%. Then the result of a particular transition is given as a percentage of the total number of transitions.

**3.3 Soft-Cube Model**

**3.3.1 Distorted Wave Solution**

The distorted wave solution is a very useful approximation for many problems and is developed in most basic textbooks on scattering theory (see reference 19). For the approximation to be applicable one must be able to separate the scattering potential into two parts where the effects of one dominate over the effects of the other. Furthermore the solution for the dominant part must be known. The weaker part of the potential is then treated as a perturbation.

The potential for the soft cube is given by equation (3.2). This potential can be written in two parts by adding and subtracting an exponential potential that is independent of the thermal motion. This results in

\[ V(z,u) = V_0 e^{-z/c} + V_0 e^{-z/c} [e^{u/c} - 1] \]

Whether this second potential can be considered as a perturbation depends upon the size of \( u \) compared to \( c \). If the ratio \( u/c \) is very small, then clearly \( V_2 \) is much smaller than \( V_1 \). Since the root-mean-square displacement is on the order of a few hundredths of an angstrom and \( c \) is about one quarter of an angstrom, it seems reasonable to assume that the second potential is small.
The solution for $V_1$ is quite simple. Since $V_1$ is independent of $u$, the wave function for the oscillator and the interaction part separate. Thus one can immediately write

$$\psi_m(z,u) = \psi_m(u) \chi_m(z)$$  \hspace{1cm} (3.43)

where $\psi_m$ is the oscillator wave function and $\chi_m(z)$ is the solution to the exponential potential $V_1$ with an incident wave vector $k_m$.

Using the distorted wave approximation we can write the T-matrix as

$$T \approx \delta_{nm} \phi_n \langle V_1 | \chi_m^{(+)} \rangle + \langle \psi_n^{(-)} | V_2 | \psi_m^{(+)} \rangle$$  \hspace{1cm} (3.44)

where $\delta_{nm}$ is the Kronecker delta function, $n$ is the final state and $m$ is the initial state. The superscripts plus and minus refer to the outgoing and incoming wave functions respectively. By substitution equation (3.44) becomes

$$T = \delta_{nm} [\phi_n \langle V_1 | \chi_m^{(+)} \rangle - \langle \psi_n^{(-)} | V_0 e^{-z/c} | \chi_m^{(+)} \rangle ] +$$

$$+ \langle \psi_n^{(-)} | e^{u/c} | \psi_m^{(+)} \rangle < \chi_n^{(-)} | V_0 e^{-z/c} | \chi_m^{(+)} >$$  \hspace{1cm} (3.45)

There are three types of integrals to evaluate. All can be put in standard forms and their values found in a straightforward manner. In doing the integrals involving the final wave vector we follow the same convention as before and use the absolute value of $k_m$ with the minus sign put in explicitly.

The first integral in equation (3.45) is

$$V_0 \int e^{-izk_m} e^{-z/c} \chi_m(z) dz$$  \hspace{1cm} (3.46)

where $k_n = k_m$ because of $\delta_{nm}$ i.e., it is an elastic term. Using this the integral is found to be

$$= - \frac{m^2 \Gamma(1 + iq_m) \text{SINH}(\nu q_m)}{2 \pi m (cB)^{2iq_m + iz}} \frac{\Gamma(1 + iz)}{\Gamma(1 + iq_m)}$$  \hspace{1cm} (3.47)

where all symbols have the same meaning as before.

The second integral is

$$\langle \chi_m^{(-)} | V_0 e^{-z/c} | \chi_n^{(+)} >$$

$$= - \frac{m^2 \Gamma(1 + iq_m) \Gamma(1 + iq_n) \text{SINH}(\nu q_m) \text{SINH}(\nu q_n)}{2 \pi m^2 (cB)^{iq_m + iq_n} (cB)^{iq_m + iq_n}} \left[ \text{SINH} \left( \frac{2 + iq_m + iq_n}{2} \right) \right]^2$$  \hspace{1cm} (3.48)
And the last matrix is

\[
\langle \psi_m^{(-1)} | e^{u/c} | \psi_n^{(+)} \rangle = \frac{-(n+m)^2}{z^2} \left( \frac{1}{2} \int_{-\infty}^{\infty} e^{M_0 \frac{u^2}{2}} \frac{u}{c} \right) \left( \frac{M_0}{\frac{u}{c}} \right)^{1/2} H_m \left( \frac{M_0}{\frac{u}{c}} \right) e^{-H_n \left( \frac{M_0}{\frac{u}{c}} \right) u} du.
\]

This can be evaluated according to the two cases:

Case (i) \( n > m \)

\[
\delta^2/4 \left( \frac{\delta}{\sqrt{2}} \right)^{n-m} L_m \left( -\delta^2/2 \right)
\]

and

Case (ii) \( m > n \)

\[
\delta^2/4 \left( \frac{\delta}{\sqrt{2}} \right)^{m-n} L_n \left( -\delta^2/2 \right)
\]

where

\[
\delta = \frac{1}{c} \sqrt{\frac{z}{M_0}}
\]

3.3.2 Thermal Average Over the Boltzmann Factor

As before we wish to include the surface temperature by averaging over the Boltzmann distribution of initial states. It is convenient to consider two cases: the elastic and the inelastic cases.

Case (i) elastic \((n = m)\)

Collecting all terms the elastic T-matrix is

\[
T_{mn}^m = \frac{A^2 \Gamma(1+i_{q_m}) \Gamma(1+i_{q_m}) \sinh(\pi q_m)}{2 \pi mc(cB) \Gamma(1+i_{q_m})} \left[ -i + q_m \left\{ e^{\delta^2/4} L_m^0 \left( -\frac{\delta^2}{2} \right) - 1 \right\} \right]
\]

and

\[
|T_{mn}^m|^2 = \left( \frac{A^2}{2m} \right)^2 4k_m^2 \left[ 1 + q_m^2 \left\{ e^{\delta^2/2} \left[ L_m^0 \left( -\frac{\delta^2}{2} \right) \right]^2 - 2 e^{\delta^2/4} L_m^0 \left( -\frac{\delta^2}{2} \right) + 1 \right\} \right].
\]

The average of this function over the Boltzmann states is carried out exactly as before and yields

19
\[<|T|^2> = \left( \frac{\hbar^2}{2m} \right)^2 4k_m^2 \left[ l + q_m^2 \left\{ e^{\frac{\delta^2}{4}} \cdot \exp \left[ \frac{z_0^2}{1-z} \right] I_0 \left[ \frac{\delta^2 \sqrt{z}}{1-z} \right] \right. \right. \\
\left. \left. + 1 \right] \right. \right. \]
\]

Case (ii) inelastic \( n \neq m \)

Again the procedure here is exactly the same as that outlined in section 3.2.3. The result is

\[<|T|^2> = \left( \frac{\hbar^2}{2m} \right)^2 \frac{\pi^2 q_n^2 \sinh(\pi q_n) \sinh(\pi q_n)(q_m^2 - q_n^2)^2}{2 \sinh^2 \left[ \frac{\pi}{2}(q_m + q_n) \right] \sinh^2 \left[ \frac{\pi}{2}(q_m - q_n) \right]} \]

\[\times \exp \left[ \frac{\delta^2 (1+z)}{2(1-z)} \right] I_{|n-m|} \left[ \frac{\delta^2 \sqrt{z}}{1-z} \right]. \quad (3.55)\]

For a later comparison it is convenient to expand equations (3.55) and (3.56) to first order in \( \delta^2 \). This is valid as long as \( \delta^2 \) is small. For gold it is about .02. Equation (3.55) to first order is

\[<|T|^2> \sim \left( \frac{\hbar^2}{2m} \right)^2 4k_m^2 \left[ l + q_m^2 \frac{\delta^2 3z}{1-z} \right]. \quad (3.57)\]

\[\sim |\phi_f V_1 |x>|^2 \left[ l + q_m^2 \frac{\delta^2 3z}{1-z} \right]. \quad (3.58)\]

Equation (3.56) to first order is

\[<|T|^2> = |\chi_n(-) V_1 |\chi_m(+) >|^2 \frac{-(n-m)}{z^2} \left[ \frac{\delta^2 \sqrt{z}}{2(1-z)} \right] |n-m| \frac{1}{\Gamma(1+|n-m|)} . \quad (3.59)\]

For \( n - m = \pm 1 \) equation (3.59) is

\[<|T|^2> = |\chi_n(-) V_1 |\chi_m(+) >|^2 \left\{ \frac{\delta^2}{2(1-z)} \right\} \text{ if } n-m = 1 \]

\[\left\{ \frac{\delta^2 z}{2(1-z)} \right\} \text{ if } n-m = 1 \quad (3.60)\]

This completes the analytic calculations for this case. The probability for the different transitions are calculated from equation (3.41) with the same normalization.
3.3.3 Linear Term Analysis

A commonly used method to get an approximate solution to the potential in equation (3.42) is to assume $u/c$ small enough that the exponential can be expanded with only the first two terms being retained. This approximation has the added advantage that a normal mode analysis may be used instead of the simple harmonic oscillator that we have used. However it has the disadvantage of being a more severe assumption. To see how it compares to the multiple phonon development we will outline the calculation and show the results for the linear term analysis.

The procedure is exactly the same as in section 3.3.1 only now the potential is

$$V(z,u) = V_0 e^{-z/c} + V_0 e^{-z/c} \left( \frac{u}{c} \right)$$

Using the distorted wave approximation as before the T-matrix is

$$T \sim \delta_{nm} \langle \phi_+ | V_0 e^{-z/c} | \chi_m^{(+)} \rangle + \langle \psi_n | \frac{u}{c} \chi_n^{(-)} | V_0 e^{-z/c} | \chi_m^{(+)} \rangle.$$  \hspace{1cm} (3.62)

By using the recursion relations for the Hermite polynomials the second matrix is

$$\langle \psi_n | \frac{u}{c} \psi_m \rangle = \delta^2 \left[ \sqrt{\frac{m!}{2^{m} \sqrt{2}}} \delta_{n,m-1} + \sqrt{\frac{m+1}{2}} \delta_{n,m+1} \right].$$ \hspace{1cm} (3.63)

Equation (3.63) clearly shows that the second term in equation (3.62) allows only plus or minus one phonon with the first term being elastic.

By averaging over the Boltzmann states we obtain the following results:

Case (i) elastic $(n = m)$

$$\langle |T|^2 \rangle = \left( \frac{\delta^2}{2m} \right) k_m^2 = \langle \phi_+ | \chi_m^{(+)} \rangle^2$$  \hspace{1cm} (3.64)

Case (ii) inelastic $(n-m = \pm 1)$

$$\langle |T|^2 \rangle = \left| \langle \chi_n^{(-)} | V_1 | \chi_m^{(+)} \rangle \right|^2 \begin{cases} \frac{\delta^2}{2(1-z)} & \text{if } n-m = 1 \\ \frac{\delta^2 z}{2(1-z)} & \text{if } n-m = -1 \end{cases}$$  \hspace{1cm} (3.65)

In the next section we discuss the comparison of these results to those in section 3.3.2.
4. NUMERICAL RESULTS AND CONCLUSIONS

4.1 Comparison of the Multiple Phonon Analysis to the Linear Analysis

As was pointed out in section 3.3.3 the linear analysis has the great advantage of being adaptable to the normal mode analysis. This is extremely important because any realistic model of the solid surface must account for the complete thermal motion. To find the conditions under which the linear analysis seems reasonable, we compare the linear and the multiple phonon equations.

For the inelastic scattering equations (3.60) and (3.65) are compared. This comparison shows that to a first order expansion in $\delta^2$ the two methods of calculation yields identical results. This means that $\delta^2$ is an extremely important controlling parameter. The linear approximation is more accurate as $\delta^2$ gets smaller.

The physical meaning of $\delta$ is very clear from its definition in equation (3.52). It is simply the average displacement of the oscillator divided by the characteristic length, $c$ of the exponential. We can then conclude that if the square of this ratio is small, one can proceed with a linear analysis. In the more general case where the complete thermal motion is considered one would use the condition

$$\frac{\langle u^2 \rangle}{c} < 1.$$  \hspace{1cm} (4.1)

In using this condition one must remember that it corresponds to the surfaces conditions and not the bulk.

For the elastic scattering we compare equations (3.57) and (3.64). Here we find that the two differ by the term

$$q_m^2 \frac{3\delta^2 z}{1-z}.$$  \hspace{1cm} (4.2)

Since $q_m^2$ is proportional to the incident energy, we have an additional condition to insure that the terms arising from $V_2$ are perturbations. The incident energy must not get too large or this term will be too large for a perturbation. In particular one should be cautious in using a Maxwellian distribution of incident energies.

Actually this problem may be avoided by investigating the origin of the terms proportional to $q_m^2$ in equation (3.55). They are corrections to the elastic term due to the thermal motion of the target. In effect they are the result of the Debye-Waller factor. This suggests that a better approximation would be to use the thermally averaged potential for $V_1$ instead of totally neglecting the thermal motion in $V_1$ as was done. That is, in equation (3.42) we used

$$V_1 = V(z,0)$$  \hspace{1cm} (4.3)

where

$$V_1 = \langle V(z,u) \rangle_T$$  \hspace{1cm} (4.4)

would have been better. Using this method the wave function in equation (3.43) would be modified to account for these additional elastic terms.
Finally we point out that the expansion to first order in $\delta^2$ also requires that $z$ is not large and in particular not close to 1 such that $1/(1-z)$ is not large. This essentially puts a restriction on the solid temperature i.e., $T_s$ should not be large.

4.2 Hard-Cube Results

The numerical results for the hard-cube are shown in tables I-IV. The entries are the probabilities (in percentages) for a given transition ($\Delta n$). A negative $\Delta n$ is the inelastic case where the gas particle loses energy to the surface and vice versa for the positive $\Delta n$.

Table I compares the transition probabilities as the surface temperature, $T_s$ is varied. As the surface temperature is increased the fraction amount of elastic ($\Delta n = 0$) scattering decreases. This is as expected because as the temperature increases, the thermal displacement increases thus making inelastic collisions more probable. In comparing the one phonon transitions, one sees that the greatest change is for the gas gaining a phonon. This means that as the surface is heated the probability for the gas gaining a phonon is increased. Again this is expected because a hotter surface has more energy to release.

Table II compares the results for three different incident energies. As the incident energy is increased, the amount of elastic scattering is decreased. A higher incident energy essentially creates a more violent collision resulting in more inelastic scattering. Here the greatest change in the probabilities is for the gas losing energy.

MacRae and Germer (20) have found experimental evidence for a decreased Debye temperature for the surface atoms due to the increased thermal displacement. For the Einstein model of the solid this would mean a decreased Einstein temperature. To see how this would affect the probabilities a comparison is shown in Table III. The results clearly show that as the Einstein temperature, $\Theta$ is decreased the inelastic scattering increases.

Table IV compares gold to tungsten. Tungsten shows much more elastic scattering than gold. This is explained by the fact that the Einstein temperature is much higher for tungsten than for gold. This is supported by the results in Table III. The results for tungsten is not as accurate as for gold because the collision time is increased by the increased Einstein temperature.

4.3 Soft-Cube Results

The numerical results for the soft-cube are given in Tables V-IX. For comparison to the hard-cube model Tables V-VIII correspond to the same conditions as those in Tables I-IV. The value for $c$ is the same as Logan and Keck (3) used. In general the soft cube shows the same trends as the hard-cube.

There are two substantial differences between the two cases. First the soft-cube shows less inelastic scattering. This is due to the fact that the exponential decelerates the gas particle more gradually and "soften" the collision. Second the $\pm 2$ phonon transition drops off much more rapidly for the soft-cube than for the hard-cube. This is probably also due to the "softening" of the collision. This means that using a linear analysis or a one phonon theory is a good approximation for the soft-cube but not for the hard-cube. The soft-cube model is the more physically reasonable model of the two so this
result is good.

Table VIII compares gold to tungsten. Again tungsten is much more elastic. In fact the elastic scattering seems too large. This could be due to the value of $c$. The same value as for gold was used. However Yamamoto and Stickney (21) found that they had to use a smaller value to get good results. In Table IX we compare the results by using both values. One immediately sees a substantial change in the probabilities. The sharper potential (i.e., smaller $c$) shows less elastic scattering. This also shows that $c$ must be known accurately to accurately calculate the transition probabilities.

4.4 General Conclusions

Within the framework of the simple model used, we can conclude that it is reasonable to neglect transitions higher than plus or minus one. The hard-cube shows substantial contribution for $\Delta n = \pm 2$ but the soft-cube is a more physically reasonable model and has a very small contribution for this transition. Even though the two phonon transition is negligible in all cases for the soft-cube, the one phonon transition shows a contribution that should be measurable. Furthermore, by controlling the surface temperature or the incident energy the one phonon intensity can be controlled with little effect of the two phonon intensity. It thus seems that helium can be an effective tool in measuring surface properties of metals following the approach used for ionic crystals by Cabrera, Celli, and Manson (22).
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   Kornelsen, E. V.

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Manson, R.  
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APPENDIX A: SCATTERING FROM AN EXPONENTIAL POTENTIAL

The exponential potential is expressed by

\[ V(z) = V_0 \ e^{-z/c} \quad \text{A-1} \]

where \( V_0 \) and \( c \) are constants. We wish to solve the wave function \( \chi \), for a particle of mass \( m \), incident from \( z \to \infty \) with energy, \( E \). The Schrodinger equation is

\[ \frac{d^2 \chi}{dz^2} + \frac{2m}{\hbar^2} \left[ E - V_0 \ e^{-z/c} \right] \chi(z) = 0 \quad \text{A-2} \]

with the boundary conditions:

1. Limit \( \chi(z) \to 0 \)
   \[ z \to -\infty \quad \text{A-3} \]
   and
   \[ -izk \ \phi \ izk \]

2. Limit \( \chi(z) \to e^{izk} + e^{-izk} \)
   \[ z \to \infty \quad \text{A-4} \]

where \( k = \sqrt{\frac{2mE}{\hbar^2}} \) and \( \phi \) is the phase shift. The first boundary condition simply expresses the fact that the particle must eventually be turned around. The second condition is essentially a normalization and as in most scattering problems we choose the incident plane wave.

By a change of variable equation A-2 can be transformed to a Bessel equation. Let

\[ \xi = 2cB \ e^{-z/2c} \quad \text{A-5} \]

and

\[ q = 2ck \quad \text{A-6} \]

where

\[ B = \sqrt{\frac{2mV_0}{\hbar^2}} \quad \text{A-7} \]

With these equation A-2 becomes

\[ \frac{d^2 \chi}{d\xi^2} + \frac{1}{\xi} \ \frac{d\chi}{d\xi} + \left[ \left( \frac{q}{\xi} \right)^2 - 1 \right] \chi = 0 \quad \text{A-8} \]

which has the solutions \( I_{-iq} \) and \( K_{iq} \). Only \( K_{iq} \) will satisfy the first boundary condition.

\( K_{iq} \) is defined by the relation (see Reference 18),

\[ K_{iq} = \frac{\pi}{2} \ \frac{I_{-iq} - I_{iq}}{i \sinh(q\pi)} \quad \text{A-9} \]
To apply the second boundary condition we must evaluate equation A-9 in the limit of large $z$ values and hence small $\xi$ values. From reference (18) we find

$$\lim_{\xi \to 0} \prod_{+i\xi}(\xi) = \frac{+i\xi - izk}{+i\xi \Gamma(+i\xi)}.$$ \hspace{1cm} A-10

Using this in equation A-9 we find

$$\lim_{z \to \infty} K_{i\xi} \to \frac{\pi}{2\sinh(q\pi)} \left[ \frac{i\xi - izk}{q \Gamma(i\xi)} + \frac{-i\xi izk}{q \Gamma(-i\xi)} \right].$$ \hspace{1cm} A-11

Then by comparison to equation A-4 we find the solution

$$x(z) = \frac{2q\Gamma(i\xi) \sinh(q\pi)}{\pi(cB)^{iq}} K_{i\xi}(2cB e^{-\xi/2c}).$$ \hspace{1cm} A-12
APPENDIX B: THE LAGUERRE POLYNOMIALS

From reference (17) we state the definition and some special properties needed in the main text.

1. Definition:

\[ L_n^\alpha(x) = \frac{\chi^n}{n!} \chi^{-\alpha} \frac{d^n}{dx^n} (e^{-\chi} \chi^{n+\alpha}) \]

\[ = \sum_{m=0}^{n} (\pm 1)^n \binom{n+\alpha}{n-m} \frac{x^m}{m!} \]

2. Some Recursion Relations:

a) \( L_n^{\alpha-1}(x) = L_n^\alpha(x) - L_{n-1}^\alpha(x) \)

b) \( \chi L_n^{\alpha+1}(x) = (n+\alpha+1)L_n^\alpha(x)-(n+1)L_{n+1}^\alpha(x) \)

c) \( (n+1)L_{n+1}^\alpha(x)-(2n+\alpha+1-\chi)L_n^\alpha(x)+(n+\alpha)L_{n-1}^\alpha(x) = 0. \)

3. Special Sum of Laguerre Polynomials:

\[ \sum_{n=0}^{\infty} \frac{n! L_n^\alpha(x) L_n^\alpha(y)}{\Gamma(n+\alpha+1)} z^n = \frac{(xyz)^{-\alpha/2}}{1 - z} \exp \left( -z \frac{x+y}{1-z} \right) I_\alpha \left( \frac{2xyz}{1-z} \right) \]

where \(|z| < 1.\)
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**TABLE I:** HARD CUBE, He/A$_{u}$, $\theta = 165^\circ$, $E = .05$ e.V., AND $\Delta n = m-n$

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<th>.1 e.V.</th>
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**TABLE II:** HARD CUBE, He/A$_{u}$, $\theta = 165^\circ$, $T_s = 300^\circ$ AND $\Delta n = m-n$
### TABLE III: HARD CUBE, $He/A_u$, $T_s = 300^\circ$, $E = .05$ e.V.
AND $\Delta n = m-n$

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### TABLE IV: HARD CUBE, $T_s = 300^\circ$, $E = .05$ e.V.,
AND $\Delta n = m-n$

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$E = .05$ eV. AND $\Delta n = m-n$

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<td>76.98</td>
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<td>3.59</td>
<td>9.77</td>
<td>11.89</td>
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<tr>
<td>2</td>
<td>.002</td>
<td>.04</td>
<td>.08</td>
<td></td>
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</tbody>
</table>

**TABLE VI:** SOFT CUBE, He/A, $\theta = 165^\circ$, $C = .26^\circ$A, 
$T_s = 300^\circ$ AND $\Delta n = m-n$

<table>
<thead>
<tr>
<th>$E$</th>
<th>$\Delta n$</th>
<th>$.025$ e.V.</th>
<th>$.05$ e.V.</th>
<th>$.1$ e.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>***</td>
<td>.02</td>
<td>.10</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>3.90</td>
<td>11.28</td>
<td>17.52</td>
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<td>89.31</td>
<td>78.88</td>
<td>70.32</td>
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<td>6.77</td>
<td>9.77</td>
<td>12.01</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>.02</td>
<td>.04</td>
<td>.06</td>
<td></td>
</tr>
</tbody>
</table>
### Table VII: Soft Cube, He/Au, $T_s = 300^\circ$, $E = 0.05$ e.V., $C = 0.26^\circ A$ and $\Delta n = m-n$

<table>
<thead>
<tr>
<th>$\Delta n$</th>
<th>$165^\circ$</th>
<th>$140^\circ$</th>
<th>$110^\circ$</th>
</tr>
</thead>
<tbody>
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<td>-2</td>
<td>0.02</td>
<td>0.06</td>
<td>0.19</td>
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<td>11.28</td>
<td>13.40</td>
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<td>2</td>
<td>0.04</td>
<td>0.07</td>
<td>0.18</td>
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</tbody>
</table>

### Table VIII: Soft Cube, $T_s = 300^\circ$, $E = 0.05$ e.V., $C = 0.26^\circ A$, AND $\Delta n = m-n$

<table>
<thead>
<tr>
<th>$\Delta n$</th>
<th>He/Au $\theta = 165^\circ$</th>
<th>He/W $\theta = 310^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>0.02</td>
<td>***</td>
</tr>
<tr>
<td>-1</td>
<td>11.28</td>
<td>2.07</td>
</tr>
<tr>
<td>0</td>
<td>78.88</td>
<td>95.25</td>
</tr>
<tr>
<td>1</td>
<td>9.77</td>
<td>2.68</td>
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<tr>
<td>2</td>
<td>0.04</td>
<td>~0.0007</td>
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</tbody>
</table>
TABLE IX: SOFT CUBE, He/W, $T_s = 300^\circ$, $E = .05$ e.V.,
$\theta = 310^\circ$ AND $\Delta n = m-n$

<table>
<thead>
<tr>
<th>$\Delta n$</th>
<th>$C = .26^\circ A$</th>
<th>$C = .13^\circ A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
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<td>7.19</td>
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<tr>
<td>1</td>
<td>2.68</td>
<td>5.62</td>
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<tr>
<td>2</td>
<td>$\sim .0007$</td>
<td>.02</td>
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</tbody>
</table>
Quantum Transition Calculations for Gas-Surface Interactions

Sisson, A. E. 26 pages 9 tables
3. Multiple Phonon Transitions 4. Helium Atom Surface Probe

It is first shown that the interaction potential between a gas atom and a solid surface with a finite temperature can be conveniently represented by a two-dimension Fourier series with the coefficients being functions of the distance between the atom and the surface*. This representation is useful and shows the basis for the one-dimensional assumption ion used in the hard and soft-cube models. Secondly the quantum mechanical analogues of the hard and soft-cube models are used to calculate the probabilities for multiple phonon transitions for the gas-surface collisions. Both analytical and numerical results show that it is feasible to use helium as a surface probe.

* While his work was in progress and the treatment of the surface potential was mostly completed a paper appeared in the literature using the same general approach. See reference 23.

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