THE VELOCITY AND DIRECTIONAL DISTRIBUTION OF SUBLIMING MOLECULES

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SYMBOLS

$F(\theta,\varphi)$	fraction of subliming molecules in an increment of solid angle $d\theta\ d\varphi$
$f(\theta,\varphi)$	probability density of θ and φ distributions
$F(\theta)$	fraction of subliming molecules in an angular increment $d\theta$
$F(\varphi)$	fraction of subliming molecules in an angular increment $d\varphi$
$f_\theta(\theta)$	probability density of θ distribution
$f_\varphi(\varphi)$	probability density of φ distribution
ΔE	potential energy difference between adsorbed molecule and free molecule
$\Delta E'$	potential energy difference between free molecule and molecule at top of potential barrier
E_I	initial energy of normal degree of freedom
E_r	energy of n-quanta transition from interior of crystal
h	Planck's constant
k	Boltzmann's constant
i	quantum number of x-oscillator
j	quantum number of y-oscillator
n	number of quanta from interior of crystal
m	mass of subliming molecule
ν	frequency of interior oscillators
ν_x	frequency of x-oscillator
ν_y	frequency of y-oscillator
P_{dV}	probability that the velocity lies between V and $V + dV$

$P_{\leq V}$	probability that the velocity is less than or equal to V
$P_{\leq\theta\leq\varphi}$	probability that the angles of a particular molecule are $\leq\theta$; $\leq\varphi$
$P_{\leq\theta}$	probability that the angle of a particular molecule is $\leq\theta$
$P_{\leq\varphi}$	probability that the angle of a molecule is $\leq\varphi$
V	velocity
θ,φ	angle in the spherical coordinate system
x,y,z	rectangular coordinates
Z	Partition function
T	absolute temperature

I. INTRODUCTION

A survey of the literature indicated very little work dealing specifically with the dynamics of subliming molecules as they leave the surface of a crystal. The thermodynamics of phase transitions deals only with the differences in the average properties of various phases at equilibria, and kinetics research is generally aimed at determining and studying rate-controlling steps, which for sublimation have not been found to be the actual ejection of the molecules from the surface.

The derivations presented here are a statistical mechanical study based on the physical model outlined in the next section. Essentially the model consists of the assumption that the molecule, in the last step before leaving the surface, is not part of the continuous plane of molecules constituting the surface, but is in an adsorbed position on the surface, as shown in figure 1. The molecule is assumed to move in three independent degrees of freedom, two parallel, and one normal to the crystal surface. The energy for sublimation is assumed to come from the interior of the crystal. In studying the specific heats of crystals Einstein (ref. 2) assumed that the energy of a crystal is contained in an assembly of quantum harmonic oscillators all of the same frequency. This approximation is retained in this paper.

In addition to the derivation of the velocity distributions, use is made of the velocity distributions to derive the directional distributions of the subliming molecules. In setting up the physical model, a potential barrier was assumed to exist which the molecule must pass over to leave the surface. It developed that both the velocity and directional

distributions are dependent upon the height of this barrier, as would be expected. Since directional distributions are more amenable to experimental measurement, they could be used as a means for determining the height of the potential barrier.

II. THE PHYSICAL MODEL

Burton, Cabrera, and Frank (ref.4) have developed a comprehensive theory of crystal growth which assumes as a mechanism the formation of monatomic ledges which grow by surface diffusion of molecules which have been adsorbed on the crystal surface. Birth and Pound, (ref. 5) have shown by thermodynamic arguments that the most likely mechanism for sublimation is the desorption of adsorbed molecules which have previously migrated from surface ledges. This mechanism for the sublimation process, together with certain assumptions about the motion of the adsorbed molecule, constitute the physical model on which the following derivations are based.

Figure 1 shows the lattice of a simple cubic crystal with a molecule of the same substance adsorbed on the surface. The adsorbed molecule may be thought of as lying in a three dimensional potential well, which will be symmetric about the normal to the surface, but whose Z dependence is unspecified. Assumptions are made about the motion of the molecule in this well which must remain unproved, although an attempt will be made to show them to be physically reasonable. The first of these assumptions is that the molecule moves in three independent orthogonal degrees of freedom. This allows the treatment of the velocity distributions in component form. Two degrees of freedom are assumed to be quantum harmonic oscillators aligned parallel to the surface along the

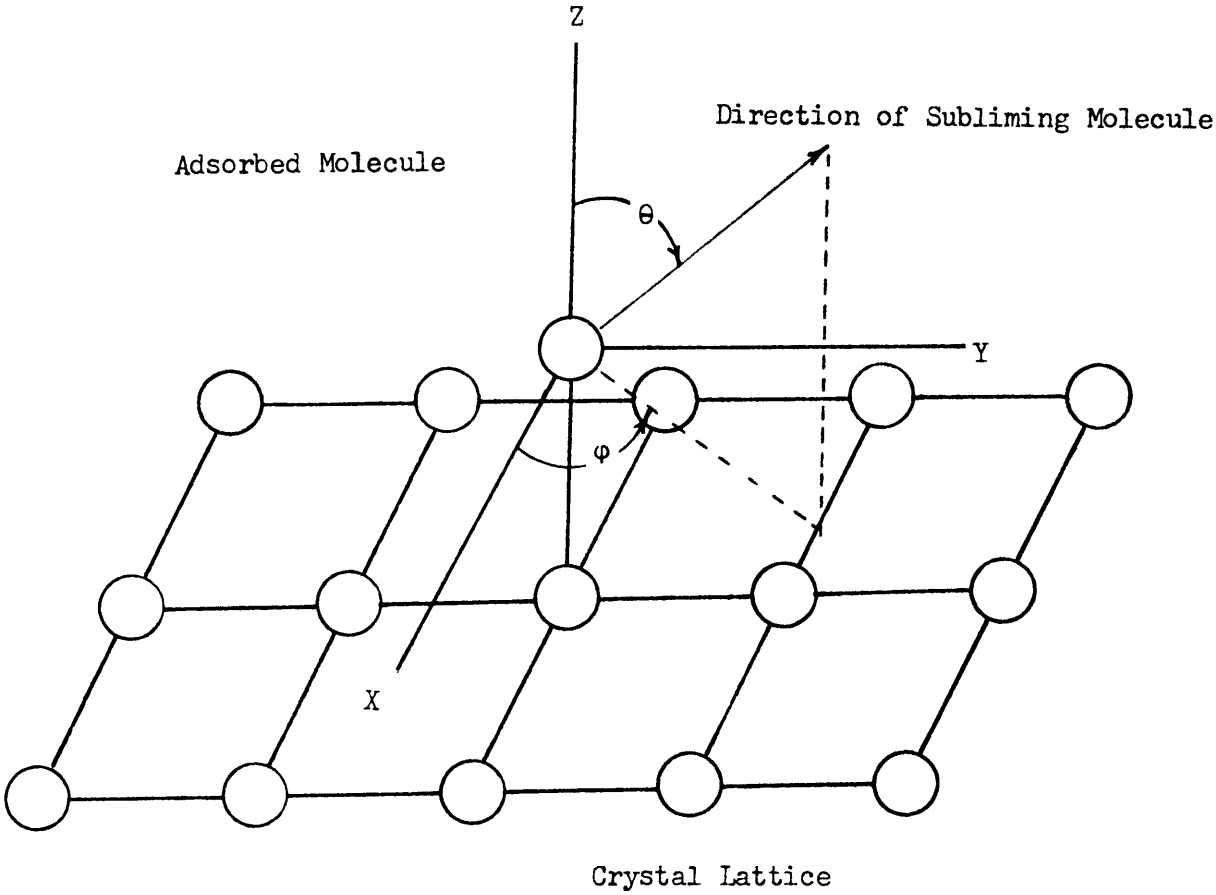

Figure 1.- Adsorbed molecule on the (100) plane of a simple cubic crystal.

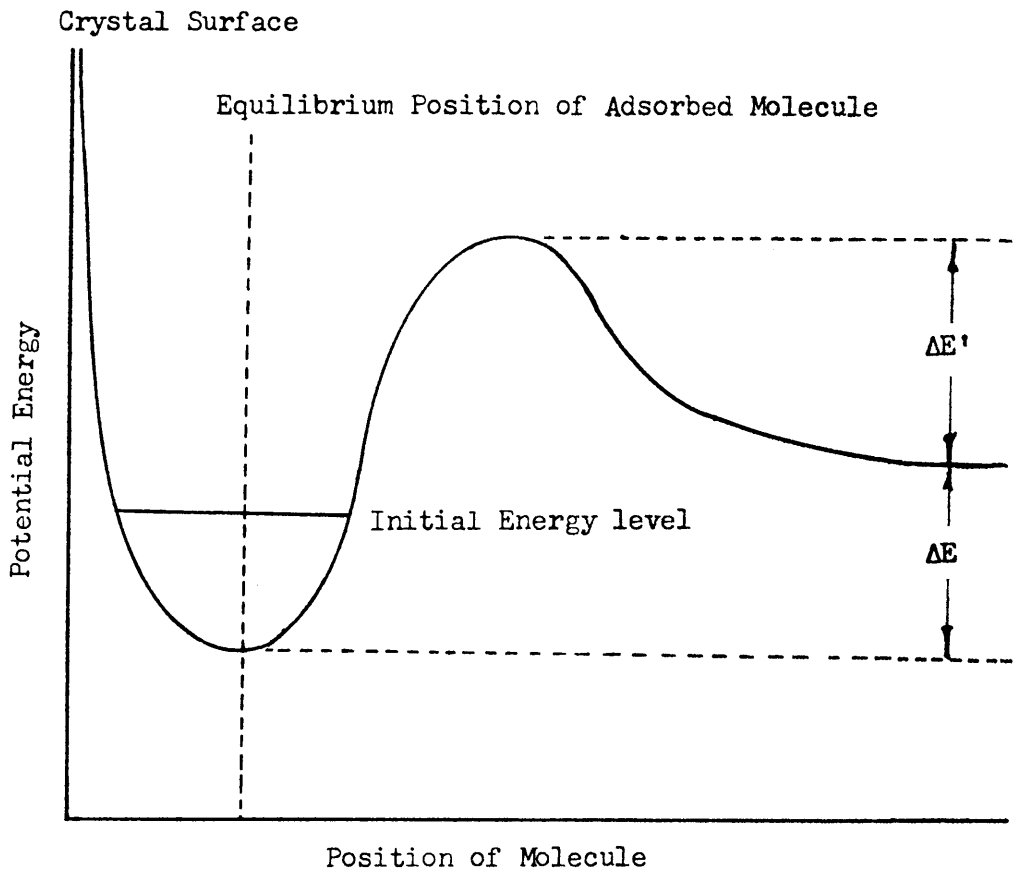

Figure 2.- Potential energy of an adsorbed molecule.

x and y axes shown in figure 1. The third is normal to the surface and the motion is unspecified. The harmonic oscillator assumption should be reasonably valid for low excitation levels, which is generally the case at temperatures below the melting point. The assumption of independence of the three degrees of freedom will be shown to have no effect on the Z-distribution. The effect of this assumption on the X and Y distributions should tend to be counteracted by symmetry. It is further assumed, as in reference 5, that it is necessary for the degree of freedom in the Z direction to have all the energy necessary for sublimation.

Figure 2 shows a rough form for the potential of the molecule as a function of its distance from the surface. No exact form is assumed for this potential, and it will be shown that the distribution functions are independent of this potential, except for the height of the barrier. The molecule has many possible energy levels in the well, and a continuum of levels above the well. Actually, a molecule outside the well is not adsorbed at all, but is a free molecule. As a mechanism for sublimation, it is assumed that the molecule is initially at some level in the well ϵ_I. In order for this molecule to sublime it must obtain energy to excite it into the continuum. It is assumed that this energy comes from the oscillators in the interior of the crystal. The velocity distribution normal to the surface is then determined by the relative transition probabilities for excitation of the adsorbed molecule to various energies in the continuum.

III. VELOCITY DISTRIBUTION OF SUBLIMING MOLECULES

The development presented here is based on the following assumptions:

(1) The molecules of the crystal may be considered as an assembly of quantum harmonic oscillators of constant frequency, except for the adsorbed molecules on the surface, which are considered as two orthogonal oscillators parallel to the surface, not necessarily of the same frequency as the internal oscillators, and one degree of freedom normal to the crystal surface, of unspecified form.

(2) All of the oscillators are at thermodynamic equilibrium, obeying Boltzmann statistics.

(3) Sublimation proceeds by excitation of the degree of freedom normal to the surface into the continuum representing a free molecule.

A. Normal to the Surface

The degree of freedom normal to the surface has some initial energy E_I. This degree of freedom receives some amount of energy E_n from the interior of the crystal, which excites it into the continuum region, and the molecule leaves the surface. The interior of the crystal is assumed to be an assembly of oscillators of frequency ν, which means the crystal can only give up discrete amounts of energy $nh\nu$, where n is any positive integer. This represents the transitions possible to the assembly of oscillators. The velocities in the z direction corresponding to these transitions are:

$$V_{z_n} = \left[\frac{2\left(nh\nu + E_I - \Delta E\right)}{m}\right]^{\frac{1}{2}} \tag{1}$$

It should be noted that for sublimation to occur, it is necessary that

$$nh\nu > \Delta E + \Delta E' - E_I \tag{2}$$

For the purpose of this derivation it will be said that the minimum value of n which produces sublimation is

$$n = \frac{\Delta E + \Delta E' - E_I}{h\nu} + \alpha \tag{3}$$

where α is a number, always less than unity, which is determined by the commensurability of $\Delta E + \Delta E' - E_I$ with $h\nu$.

The velocity distribution function is defined as $u\left(V_z\right)$ such that:

$$P_{dV_z} = u\left(V_z\right) dV_z \tag{4}$$

where P_{dV_z} is the probability that a molecule has a velocity between V_z and $V_z + dV_z$. Therefore

$$u\left(V_z\right) = \frac{d}{dV_z}\left(P_{\leq V_z}\right) \tag{5}$$

$P_{\leq V_z}$ is determined by summing the probabilities of all velocities up to V_z. From (3):

$$P_{V_z} = \sum_{V_z = \left(\frac{2\left[\Delta E' + \alpha h\nu\right]}{m}\right)^{\frac{1}{2}}}^{V_z} P_{V_{z_n}}$$

where $P_{V_{z_n}}$ is the probability that a molecule has a particular velocity V_n as given in equation (1).

In order to evaluate the summation in (6), it is desirable to use the index n. From equations (1) and (5), the lower and upper limits of summation are:

$$n = \frac{\Delta E' + \Delta E - E_I}{h\nu} + \alpha \tag{7}$$

and

$$n = \frac{\frac{1}{2}mV_z^2 - E_I + \Delta E}{h\nu} \tag{7a}$$

The probability that a subliming molecule has a velocity V_{z_n} is the same as the probability that the molecule will be excited into the continuum by an energy transition $nh\nu$. According to Boltzmann statistics, the relative probability for a transition of energy E_n is:

$$P_R = \exp\left(\frac{-E_n}{kT}\right) \tag{8}$$

The absolute probability of this transition is:

$$P = \frac{\exp\left(\frac{-E_n}{kT}\right)}{\sum_i \exp\left(\frac{-E_i}{kT}\right)} \tag{9}$$

where the summation is over all the possible transitions.

The transitions which will produce sublimation are those for which n is from $\frac{\Delta E' + \Delta E - E_I}{h\nu} + \alpha$ to infinity so that

$$P_{V_n} = \frac{\exp\left(-\frac{nh\nu}{kT}\right)}{\sum_{i=\frac{\Delta E'+\Delta E-E_I}{h\nu}+\alpha}^{\infty} \exp\left(-\frac{ih\nu}{kT}\right)} \tag{10}$$

Evaluating the summation

$$P_{V_{z_n}} = \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right] \exp\left(-\frac{[n - \alpha]k\nu - \Delta E' - \Delta E + E_I}{kT}\right) \tag{10a}$$

Therefore, from (6), (7), (7a), and (10a)

$$P_{\leq V_z} = \sum_{n=\frac{\frac{1}{2}mV_{z_n}^2 - E + \Delta E}{h\nu}}^{\frac{\Delta E'+\Delta E-E_I}{h\nu}+\alpha} \left[1 - \exp\left(-\frac{h\nu}{kT}\right)\right] \exp\left(-\frac{[n - \alpha]h\nu - \Delta E' - \Delta E + E_I}{kT}\right)$$

$$V_{z_n} \leq V_z \leq V_{z_{n+1}} \tag{11}$$

$P_{\leq V_z}$ must be differentiated with respect to V_z to obtain $u(V_z)$ (see eq. (5)). However, $P_{\leq V_z}$ as defined in (11) is not a continuous function of V_z. By evaluating the summation, the following approximation is made:

$$P_{\leq V_z} \approx 1 - \exp\left[-\frac{\frac{1}{2}mV_z^2 - \Delta E' + (1 - \alpha)h\nu}{kT}\right] \tag{11a}$$

This is actually the smooth curve which approximates the multistep function expressed in (11), and its derivative is the average derivative of $P_{\leq V_z}$ over an increment $\Delta V_z \approx \frac{h\nu}{mV_z}$. Therefore

$$u\left(V_z\right) = \frac{dP_{\leq V_z}}{dV_z} = \frac{mV_z}{kT}\exp\left[-\frac{\frac{1}{2}mV_z^{\,2} - \Delta E' + (1 - \alpha)h\nu}{kT}\right] \tag{12}$$

B. Parallel to the Surface

It is assumed that all of the energy of the x and y oscillators produces velocities in the x and y directions, respectively. The problem then becomes that of determining the energy distributions of these oscillators. The same method as used for the z distribution is used here.

The energy levels of the x oscillator are:

$$E_i = \left(i + \frac{1}{2}\right)h\nu_x \qquad i = 0,1,2,3,\ldots \tag{13}$$

$$P_{\leq V_x} = \sum_{V_{x_i}=\left(\frac{h\nu_x}{m}\right)^{1/2}}^{V_x} P_{V_{x_i}} \equiv \sum_{i=0}^{\frac{1}{2}\frac{mV_x^{\,2}}{h\nu_x} - \frac{1}{2}} \left[\frac{\exp\left(-\frac{\left(i + \frac{1}{2}\right)h\nu_x}{kT}\right)}{Z_x}\right] \tag{14}$$

where Z_x is the partition function of the x oscillator, i.e., the summation of the relative probabilities of all the energy levels.

$$Z_x = \sum_{i=0}^{\infty} \exp\left(-\left(i + \frac{1}{2}\right)\frac{h\nu_x}{kT}\right) \tag{15}$$

Evaluating the summation,

$$Z_x = \frac{\exp\left(-\frac{1}{2}\frac{h\nu_x}{kT}\right)}{1 - \exp\left(-\frac{h\nu_x}{kT}\right)} \tag{15a}$$

Therefore from (14) and (15a)

$$P_{\leq V_x} = \sum_{i=0}^{\frac{1}{2}\frac{mV_x^2}{h\nu_x} - \frac{1}{2}} \left[1 - \exp\left(-\frac{h\nu_x}{kT}\right)\right] \exp\left(-i\frac{h\nu_x}{kT}\right) \tag{16}$$

$$P_{\leq V_x} = 1 - \exp\left(-\frac{\frac{1}{2}mV_x^2 + \frac{1}{2}h\nu_x}{kT}\right) \tag{16a}$$

$$u_x\left(V_x\right) = \frac{d}{dV_x}\left(P_{\leq V_x}\right) = \frac{mV_x}{kT}\exp\left(-\frac{\frac{1}{2}mV_x^2 + \frac{1}{2}h\nu_x}{kT}\right) \tag{17}$$

Likewise:

$$u_y\left(V_y\right) = \frac{mV_y}{kT}\exp\left(-\frac{\frac{1}{2}mV_y^2 + \frac{1}{2}h\nu_y}{kT}\right) \tag{18}$$

IV. DIRECTIONAL DISTRIBUTION

The direction of a molecule leaving the surface is defined by two angles in polar spherical coordinates, θ and φ as shown in figure 1.

Two approaches are possible to the analysis of the directional distribution, differing in the way that the directional distribution function is defined. One approach is to consider the fraction of the molecules in an increment of solid angle $d\theta\ d\varphi$:

$$F(\theta,\varphi) = f(\theta,\varphi)d\theta\ d\varphi \tag{1}$$

The directional distribution function is $f(\theta,\varphi)$, the probability density of the molecules in the (θ,φ) direction. If $P_{\leq\theta,\leq\varphi}$ is the fraction of the molecules lying in a solid angle $0 - \theta$, $0 - \varphi$; then

$$f(\theta,\varphi) = \frac{\partial^2}{\partial\theta\ \partial\varphi}\left(P_{\leq\theta,\leq\varphi}\right) \tag{2}$$

The second approach, which will be used here, is to consider the θ and φ distributions separately. The fractions of the molecules in angular increments $d\varphi$ and $d\theta$ are:

$$F(\varphi) = f_{\varphi}(\varphi)d\varphi \tag{3}$$

$$F(\theta) = f_{\theta}(\theta)d\theta \tag{3a}$$

f_{φ} and f_{θ} are the angular distribution functions for φ and θ, respectively.

$$f_\varphi = \frac{d}{d\varphi}\left(P_{\leq\varphi}\right) \tag{4}$$

$$f_\theta = \frac{d}{d\theta}\left(P_{\leq\theta}\right) \tag{4a}$$

The analysis will consist of evaluating f_φ and f_θ as given in equations (4) and (4a) by using the velocity distributions previously derived. f_φ and f_θ are determined by V_x, V_y, and V_z, since:

$$\tan \varphi = \frac{V_y}{V_x} \tag{5}$$

$$\tan \theta = \frac{\left(V_x^2 + V_y^2\right)^{1/2}}{V_z} \tag{5a}$$

A. φ Distribution

From equation (5):

$$P_{\leq\varphi} = P_{V_y \leq V_x \tan \varphi} \tag{6}$$

For a specific value of V_x:

$$P_{V_y \leq V_x \tan \varphi} = \int_{\left(\frac{h\nu_y}{m}\right)^{1/2}}^{V_x \tan \varphi} u\left(V_y\right) dV_y \tag{7}$$

For all values of V_x

$$P_{V_y \leq V_x \tan \varphi} = \int_{\left(\frac{h\nu_x}{m}\right)^{1/2}}^{\infty} \int_{\left(\frac{h\nu_y}{m}\right)^{1/2}}^{V_x \tan \varphi} u\left(V_x\right) u\left(V_y\right) dV_y \, dV_x \tag{8}$$

From equations (6) and (8), and the velocity distribution functions of the preceding section:

$$P_{\leq\varphi} = \int_{\left(\frac{h\nu_x}{m}\right)^{1/2}}^{\infty} \int_{\left(\frac{h\nu_y}{m}\right)^{1/2}}^{V_x \tan\varphi} \frac{mV_x}{kT} \times$$

$$\frac{mV_y}{kT} \exp\left(-\frac{\frac{1}{2}mV_x^2 + \frac{1}{2}h\nu_y}{kT}\right) \exp\left(-\frac{\frac{1}{2}mV_y^2 + \frac{1}{2}h\nu_y}{kT}\right) dV_y \, dV_x \tag{9}$$

Evaluating the integrals:

$$P_{\leq\varphi} = \exp\left(-\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu_x}{kT}\right)\left\{\exp\left(-\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu_x}{kT}\right) - \right.$$

$$\left. \frac{1}{1 + \tan^2\varphi} \exp\left(-\frac{1}{2}\frac{h\nu_x}{kT}\left[1 + \tan^2\varphi\right]\right)\right\} \tag{10}$$

$$f_\varphi \equiv \frac{d}{d\varphi}\left(P_{\leq\varphi}\right) = \exp\left(-\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu_x}{kT}\right)\left\{2 \sin\varphi \cos\varphi + \right.$$

$$\left. \frac{h\nu_x}{kT} \tan\varphi\right\} \exp\left(-\frac{1}{2}\frac{h\nu_x}{kT}\left[1 + \tan^2\varphi\right]\right) \tag{11}$$

At high temperatures, $h\nu_x \ll kT$; $h\nu_y \ll kT$, making

$$\exp\left(-\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu_x}{kT}\right) \cong 1 \tag{12}$$

and for values of φ not close to $\pi/2$

$$\exp\left(-\frac{1}{2}\frac{h\nu_x}{kT}\left[1 + \tan^2\varphi\right]\right) \cong 1 \tag{12a}$$

and

$$\frac{h\nu_x}{kT} \tan \varphi \ll 2 \sin \varphi \cos \varphi \tag{12b}$$

Therefore at high temperatures:

$$f_\varphi \cong 2 \sin \varphi \cos \varphi \tag{13}$$

The same result is obtained by the more involved method of evaluating:

$$P_{\leq\varphi} = \sum_{Q_{i,j}=0}^{\varphi} P_{\varphi_{i,j}} \tag{14}$$

where $P_{\varphi_{i,j}}$ is the probability that $\varphi = \varphi_{i,j}$ corresponding to

$$V_x = \left[\frac{2\left(i + \frac{1}{2}\right)h\nu_x}{m}\right]^{1/2} \tag{15}$$

and

$$V_y = \left[\frac{2\left(j + \frac{1}{2}\right)h\nu_y}{m}\right]^{1/2} \tag{15a}$$

B. θ Distribution

From equation (5a)

$$P_{\leq\theta} = P_{\left(V_x{}^2+V_y{}^2\right)^{1/2} \leq V_z \tan \theta} \tag{16}$$

For specific values of V_y and V_z; V_x unknown:

$$P_{\left(V_x^2+V_y^2\right)^{1/2} \leq V_z \tan\theta} = P_{V_x \leq \left(V_z^2 \tan^2\theta - V_y^2\right)^{1/2}}$$

$$= \int_{\left(\frac{h\nu_x}{m}\right)^{1/2}}^{\left(V_z^2 \tan^2\theta - V_y^2\right)^{1/2}} u\left(V_x\right) dV_x \qquad (17)$$

For a specific value of V_z; V_x and V_y unknown:

$$P_{\left(V_x^2+V_y^2\right)^{1/2} \leq V_z \tan\theta} = \int_{\left(\frac{h\nu_y}{m}\right)^{1/2}}^{V_z \tan\theta} \int_{\left(\frac{h\nu_x}{m}\right)^{1/2}}^{\left(V_z^2 \tan^2\theta - V_y^2\right)^{1/2}} u\left(V_y\right) u\left(V_x\right) dV_x \, dV_y \qquad (18)$$

In general $\left(V_x, V_y, V_z \text{ unknown}\right)$

$$P_{\leq\theta} = \int_{\left(\frac{2\left[\Delta E' + \alpha h\nu\right]}{m}\right)}^{\infty} \int_{\left(\frac{h\nu_y}{m}\right)^{1/2}}^{V_z \tan\theta} \int_{\left(\frac{h\nu_x}{m}\right)^{1/2}}^{\left(V_z^2 \tan^2\theta - V_y^2\right)^{1/2}} u\left(V_z\right) u\left(V_y\right) u\left(V_x\right) dV_x \, dV_y \, dV_z \qquad (19)$$

Substituting the velocity distribution functions and integrating

$$P_{\leq\theta} = \exp\left(-\frac{\frac{1}{2}h\nu_x + \frac{1}{2}h\nu_y + \frac{1}{2}h\nu}{kT}\right)\left\{\exp\left(-\frac{\frac{1}{2}h\nu_x + \frac{1}{2}h\nu_y + \frac{1}{2}h\nu}{kT}\right) + \right.$$

$$\left[\frac{1}{2}\frac{h\nu_y}{kT}\exp - \frac{1}{2}\frac{h\nu}{kT} - \exp\left(-\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu}{kT}\right)\right]\cos^2\theta \exp\left(-\frac{\left[\Delta E' + \alpha h\nu\right]\tan^2\theta}{kT}\right) -$$

$$\left.\sin^2\theta \exp\left(-\frac{1}{2}\frac{h\nu}{kT}\right)\left[\frac{\left(\Delta E' + \alpha h\nu\right)}{kT} + \cos^2\theta\right]\exp\left(-\frac{\left(\Delta E' + \alpha h\nu\right)\tan^2\theta}{kT}\right)\right\} \qquad (20)$$

$$f_\theta \equiv \frac{d}{d\theta}\left(P_{\leq\theta}\right) = \exp\left(-\frac{\frac{1}{2}h\nu + \frac{1}{2}h\nu + \frac{1}{2}h\nu}{kT}\right)\left\{\left[\left(\frac{1}{2}\frac{h\nu_y}{kT}\exp\left[-\frac{1}{2}\frac{h\nu}{kT}\right] - \right.\right.\right.$$

$$\left.\exp\left[\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu}{kT}\right]\right)\cos^2\theta - \exp\left(-\frac{1}{2}\frac{h\nu}{kT}\right)\left(\frac{[\Delta E' + \alpha h\nu]}{kT} + \right.$$

$$\left.\left.\cos^2\theta\right)\sin^2\theta\right]\left[-2\tan\theta\sec^2\theta\frac{(\Delta E' + \alpha h\nu)}{kT}\right] -$$

$$\frac{1}{2}\frac{h\nu_y}{kT}\exp\left(-\frac{1}{2}\frac{h\nu}{kT}\right) - \exp\left(-\frac{\frac{1}{2}h\nu_y + \frac{1}{2}h\nu}{kT}\right) 2\sin\theta\cos\theta -$$

$$2\sin\theta\cos\theta\exp\left(-\frac{1}{2}\frac{h\nu}{kT}\right)\left(\frac{[\Delta E' + \alpha h\nu]}{kT} + \cos^2\theta\right) +$$

$$\left.2\sin^3\theta\cos\theta\exp\left(-\frac{1}{2}\frac{h\nu}{kT}\right)\right\}\exp\left(-\frac{[\Delta E' + \alpha h\nu]\tan^2\theta}{kT}\right) \qquad (21)$$

Making the same high temperature approximations as in the φ distribution

$$f_\theta = \left\{2\tan\theta\frac{\Delta E'}{kT} + 2\tan\theta\sec^2\theta\sin^2\theta\left[\frac{\Delta E'}{kT} + \cos^2\theta\right]\frac{\Delta E'}{kT} + \right.$$

$$\left.2\sin\theta\cos\theta\left[1 - \frac{\Delta E'}{kT} - \cos^2\theta\right] + 2\sin^3\theta\cos\theta\right\}\exp\left(\frac{-\Delta E'\tan^2\theta}{kT}\right) \qquad (22)$$

For the case of no potential barrier ($\Delta E' = 0$) and $\theta \neq \pi/2$:

$$f_\theta = 2\sin\theta\cos\theta - 2\sin\theta\cos^3\theta + 2\sin^3\theta\cos\theta \qquad (23)$$

V. DISCUSSION OF THEORETICAL RESULTS

The derived velocity distribution functions as given by equations 12, 17, and 18 differ from the Maxwellian distribution function for gas molecules in the coefficients of the exponential term, and for $u\left(V_z\right)$, in the appearance of $\Delta E'$, which in effect, serves to shift the energy coordinate of the function to account for the existence of a minimum velocity. For $\Delta E' = 0$, the average normal component of the velocity is approximately $\left(\frac{2kT}{m}\right)^{1/2}$, compared to approximately $\left(\frac{kT}{m}\right)^{1/2}$ for a Maxwellian distribution.

It is of interest that the velocity distribution normal to the surface does not depend on the original energy of the molecule before being excited into the continuum. This is because of the property of harmonic oscillators that the energy distribution of all oscillators having energy greater than some energy E is the same as the distribution for the entire assembly with an extra energy E added to each oscillator.

The directional distribution functions are of interest in part because of the simplicity of the final forms. Of more practical importance is the dependence of the θ distribution on $\Delta E'$, as shown by equation 22. This affords a comparatively easy method for determining $\Delta E'$ experimentally.

VI. CONCLUSIONS

The following results have been obtained from this derivation of the velocity and directional distributions of subliming molecules:

(1) Equations for the velocity distributions normal and parallel to the surface as functions of temperature, and for the normal distribution, function of the potential barrier to sublimation.

(2) Using the velocity distributions, equations for the directional distributions.

(3) The average velocity normal to the surface is different from the average velocity of gas molecules normal to the surface at the same temperature.

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ABSTRACT

Expressions are derived for the velocity distributions of subliming molecules based on the assumption that the molecule, immediately prior to sublimation, is in an adsorbed position on the surface of the crystal, with three degrees of freedom. It is assumed that a quantum of energy from an assembly of quantum harmonic oscillators, representing the interior of the crystal, excites the adsorbed molecule so that it leaves the surface. The resulting expressions gave a root mean square velocity of the square root of 2 times that of a Maxwillian distribution. The derived velocity distributions were used to obtain directional distribution functions.