Maxwell versus Non-Maxwell Velocity Distributions for Molecules Emitted from a Liquid Surface

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The nature of the velocity distribution for molecules emitted from a liquid surface is considered, and the angular dependence of the sticking coefficient for molecules striking the liquid surface is calculated with allowance for the presence of thermally excited capillary waves. Of the various forms of Maxwell distribution that have been assumed to apply to the molecules emitted from a gas–liquid interface, the speed distribution for molecular effusion is most appropriate, but the available experimental data do not allow us to discriminate between this function and "floating" forms of the ordinary Maxwell distribution of speeds. The distribution function for effusion, which is the one normally used in studies of the gas–solid interface, includes a cos θ factor, where θ is the angle between the velocity vector and the normal to the surface. Our work on the kinetics of emission from the liquid surface indicates that the factor should be cos^2 θ for molecules emitted from the liquid. This angular factor has a significant effect on the angular dependence of the sticking coefficient α. Comparisons of the observed and calculated angular dependence of α at high collision energy clearly favor the form with the cos^2 θ factor over the form with cos θ.

Introduction

The term "Maxwell distribution" describes the equilibrium distribution of velocities and kinetic energies of molecules in the gas phase when they are far from the walls of the containing vessel, the condition "far from the walls" applying when the walls are not in a state of complete chemical and thermal equilibrium with the gas. For the distribution of speed or velocity v there are three important forms of the distribution function, namely, the distribution of velocities (1) in the range v to $v +$ dv, i.e., (v_x, v_y, v_z) to $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$, the distribution of molecular speeds (2), irrespective of direction, and the distribution of speeds (3) for molecules crossing an arbitrary plane into a solid angle dω:

$$f(v)\, dv_x\, dv_y\, dv_z = \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mv^2/2RT}\, dv_x\, dv_y\, dv_z \quad (1)$$

$$f(v)\, dv = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2\, e^{-Mv^2/2RT}\, dv \quad (2)$$

$$f(v)\, d\omega\, dv = \frac{1}{2\pi}\left(\frac{M}{RT}\right)^2 v^3 e^{-Mv^2/2RT} \cos\theta\, d\omega\, dv \quad (3)$$

This last equation applies also to molecules effusing through a small hole (diameter small compared with the mean free path) into a vacuum.[1] The average kinetic energy given by distribution (3) is 2RT per mole; distributions (1) and (2) correspond to an average kinetic energy of 3RT/2 per mole. In general, distributions 1 and 2 are appropriate when the quantity of interest is a number density and distribution 3 is appropriate when the quantity of interest is a molecular flux. However, the distinction can be a subtle one.

The velocity distribution for molecules leaving the surface of a liquid is generally assumed to be the Maxwell distribution for a gas at the temperature of the liquid surface. Often this assumption derives ultimately from the discussion given by Schrage.[2] Alternatively, the same position can be reached on

the basis of consideration of the motion of gas molecules that have traversed a force-field, as described, for example, in the book by Kennard.[1] However, there is little uniformity in the choice of which Maxwell distribution to use. Studies based on solving the Boltzmann equation for the region above and adjacent to the liquid surface[3–12] have used the velocity distribution of eq 1, which is plotted as curve 0 in Figure 1a. Faubel et al.[13] fitted the results of their time-of-flight measurements on molecules evaporating radially from a liquid jet to a "floating" variant of eq 2 (although the discussion by Anderson,[14] to which these authors refer, relates to the motion of molecules within a gaseous jet). Equation 2 is plotted as curve 2 in Figure 1a. In their numerical simulation of the experiments of Faubel et al., Sibold and Urbassek[15] assumed the distribution function of eq 1 for molecules leaving the surface but inserted a factor v before the exponential for the molecules contributing to the flux away from the surface. The resulting distribution is plotted as curve 1 in Figure 1a. Studies of the trapping/desorption of gas molecules at a solid surface[16–20] use the distribution given by eq 3, which is plotted (for a fixed value of θ) as curve 3 in Figure 1a. The difference between curves 2 and 3 appears quite significant, but if curve 2 is permitted to "float" until its maximum coincides with that of curve 3, as in Figure 1b, the difference is seen to be too small to be detected by experiments where the precision is of the order of a few percent. Hansson and Holmlid[19] observed what they describe as "nearly Maxwell–Boltzmann" velocity distributions of the form (3) for Cs atoms leaving a hot, graphite-covered, iridium surface. Feng and Lifshitz[20] measured kinetic energies of monomers and dimers of formic acid evaporating from small proton-bound clusters (up to eight formic acid and two water molecules per cluster) and obtained best-fit values close to unity for the power of v before the exponent, i.e., distributions close to what Sibold and Urbassek assumed for molecules leaving a liquid surface. However, although this result is certainly very interesting, it is probably irrelevant to the problem of molecules
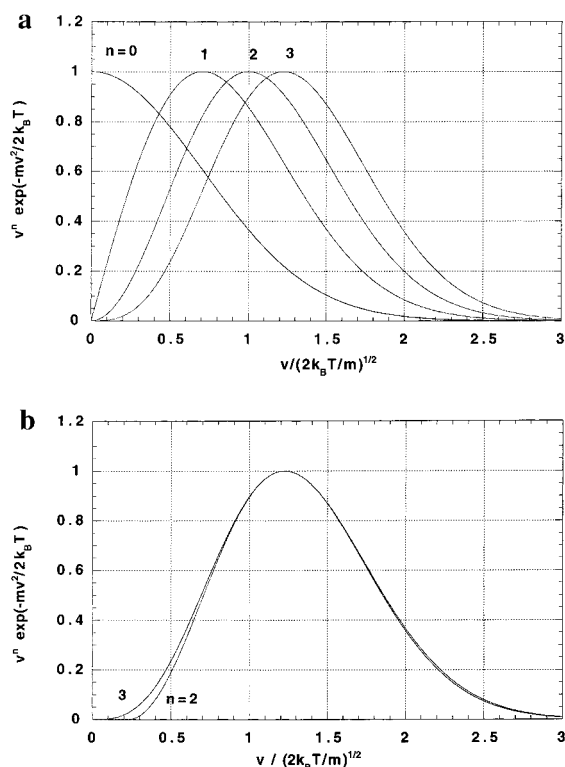
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Figure 1. (a) Forms of Maxwell distribution: curve 0, the Maxwell distribution of velocities v (eq 1); curve 1, the distribution with a weighting factor v; curve 2, with weighting factor v^2 (eq 2); curve 3, with weighting factor v^3 (eq 3). (b) Comparison of curves 2 and 3, where curve 2 has been moved so the maxima coincide.

evaporating from the surface of a bulk liquid. Faubel et al.'s explanation for the unusually high kinetic energies that they found for acid dimers evaporating from a water surface does not depend on the form of velocity distribution assumed, and again the data do not permit us to distinguish between different forms of distribution.

If we assume that the molecules leaving a small area S of liquid or solid surface do have a Maxwell distribution of speeds and consider the situation from the viewpoint of an observer located in the gas phase at a distance from S much less than one mean free path, it is apparent that such an observer could not distinguish between the emission from the surface and the emission from a small hole of area S communicating with a large volume of gas at a pressure sufficient to generate the observed flux from the surface. It follows that the correct form of Maxwell distribution to use is the one given by eq 3. However, this involves the prior assumption that the Maxwell distribution does apply to molecules escaping from the surface of a liquid.

In a previous paper from this laboratory[21] the process of evaporation of a molecule from the surface of a liquid was treated in the framework of statistical reaction-rate theory, leading to the conclusion that the evaporating molecules do not conform to any of the Maxwell distributions given above. The differences from the distributions (1) and (2) are considerable, but the difference from distribution (3) is relatively small, amounting only to replacement of a cos θ factor by cos² θ. Further, the difference in the angular dependence from that of distribution (3) is expected to become blurred in practice because of the presence of thermally excited capillary waves.[22] Here it is interesting to note that Manson, Rubahn, and co-workers,[23,24] who have measured translational energy distributions for Na atoms photodesorbed from solid sodium surfaces, report both

non-Maxwellian velocity distributions and cosine-squared angular distributions. However, their experimental system differs significantly from an evaporating liquid, and the role of surface vibrations in their model is to scatter atoms that are being photodesorbed, whereas in our model[21] it is the accumulation of vibrational energy in a critical coordinate that actually causes evaporation. In the present paper we extend our previous calculations to include the effect of random variations in the local slope of the liquid surface, with the primary aim of finding whether it is possible to distinguish between the Maxwell and non-Maxwell distributions on the basis of existing experimental data.

Deductions from Rate Constant Calculations

When we regard the surface membrane of a liquid as a large molecule whose rate of unimolecular decomposition, i.e., evaporation of one of its constituent units, can be treated by statistical reaction-rate theory, the rate constants $k(\epsilon)$ and $k(T)$ for emission at right angles to a planar liquid surface, where ϵ is the excess kinetic energy in the critical coordinate for escape and $k(T)$ is the thermal average over ϵ, are found to be[21]

$$k(\epsilon) = (\epsilon/h) \exp(-[\epsilon + q]/k_BT) \qquad (4)$$

and

$$k(T) = (k_BT/h) \exp(-q/k_BT) \qquad (5)$$

Motion parallel to the surface and internal degrees of freedom such as vibration and rotation of the departing molecules are disregarded at this stage of the calculation; h is Planck's constant, q is the latent heat of vaporization per molecule, and k_B is Boltzmann's constant. The ratio of $k(\epsilon)$ to $k(T)$ amounts to a distribution function $f(\epsilon)$ for the kinetic energy of the emitted molecules. With this distribution function, the average energy of molecules emitted at right angles to a flat liquid surface is found to be $2k_BT$,[21] which is the same as the average energy of gas-phase molecules crossing an arbitrary plane in the gas.[1]

Because the critical coordinate for escape is at right angles to the local surface, it is only kinetic energy in this coordinate that is effective in overcoming the potential barrier provided by the latent heat q. In terms of the total kinetic energy E for molecules emitted at an angle θ to the normal, the expression for $k(\epsilon)$ therefore becomes

$$k(E,\theta) = (E \cos^2\theta/h) \exp(-[E + q]/k_BT) \qquad (6)$$

When we integrate over dE, the cos² θ factor of eq 6 carries over into the expression for $k(T)$, with the result that the average kinetic energy is $2k_BT$ for molecules emitted at *any* angle θ to the normal This cos² θ factor also affects the angular dependence of the sticking coefficient for molecules colliding with the surface, as described in the next section.

Corresponding results for the intensities of effusive streams striking and leaving a flat liquid surface are given in Table 1. The intensity I is measured in molecules per unit area per second crossing an imaginary plane that is parallel to the local liquid surface and located at a distance above the surface much less than the mean free path in the gas. Expressions that contain θ have been integrated over the azimuthal angle ϕ and are to be integrated over sin θ dθ. Expressions that contain E are to be integrated over dE. Molecular concentrations are n_v per unit volume in the gas and n_s per unit area of the liquid surface, q is the enthalpy of vaporization per molecule, the mean speed $\sqrt{(8k_BT/\pi m)}$ is written as c, and the other symbols have their

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TABLE 1: Comparison of Intensity Formulas for Emission from a Plane Liquid Surface and for Impact on the Liquid by Gaseous Effusion through a Nearby Plane Parallel to the Local Surface[a]

quantity	emitted from liquid surface	arriving from gas
$I(E, \theta)$	$(3n_s E \cos^2 \theta / hk_B T)$ $\exp(-[E+q]/k_B T)$	$(n_v cE \cos\theta / 2k_B^2 T^2)$ $\exp(-E/k_B T)$
$I(E)$	$(n_s E/hk_B T) \exp(-[E+q]/k_B T)$	$(n_v cE/4k_B^2 T^2)$ $\exp(-E/k_B T)$
$I(\theta)$	$(3n_s \cos^2 \theta k_B T/h)$ $\exp(-q/k_B T)$	$n_v c \cos \theta / 2$
I_{total}	$(n_s k_B T/h) \exp(-q/k_B T)$	$n_v c/4$
$I(E,\theta)/I_{total}$	$(3E \cos^2 \theta / k_B^2 T^2)$ $\exp(-E/k_B T)$	$(2E \cos \theta / k_B^2 T^2)$ $\exp(-E/k_B T)$
$I(E)/I_{total}$	$(E/k_B^2 T^2) \exp(-E/k_B T)$	$(E/k_B^2 T^2)$ $\exp(-E/k_B T)$
$I(\theta)/I_{total}$	$3 \cos^2 \theta$	$2 \cos \theta$

[a] The number of molecules per unit area of surface is n_s; the number per unit volume of gas is n_v; c is the mean speed $\sqrt{(8k_B T/\pi m)}$. Factors of dE and $\sin \theta \, d\theta$ have been omitted from results that depend on E and θ, respectively. Expressions in terms of velocity v instead of energy E can be obtained by substituting $E = mv^2/2$ and $dE = mv \, dv$.

usual meanings. The essential difference from a Maxwell distribution of the distribution functions $I(E,\theta)$ and $I(\theta)$, which characterize molecules emitted from the liquid surface, is seen to reside in the angular factor.

Equation 6 shows how the rate of emission varies with the deviation from the normal for a fixed energy E. It is also of interest to calculate the variation of the rate with angle θ for a fixed amount of energy ϵ in the critical coordinate. This amounts to considering how eq 4, which was derived by calculating the flow of energy among only those vibrational modes that are at right angles to the surface membrane, is modified when motion parallel to the surface is introduced. Inclusion of motion parallel to the surface affects the direction in which the molecules are emitted and also affects the Boltzmann factor in the resulting rate expression, but it cannot affect the total rate of emission if the amount of energy in the critical coordinate remains the same. Hence we can write

$$k(\epsilon,\theta) = A\frac{\epsilon}{h}\exp(-[\epsilon/k_B T \cos^2 \theta + q/k_B T]) \qquad (7)$$

where A is a quantity, independent of θ, whose value is fixed by the requirement that the integral of $k(\epsilon,\theta)$ over $\sin \theta \, d\theta$ must return the right-hand side of eq 4. This gives

$$A = 1/(1 + \exp(\epsilon/k_B T)[\text{erf}(\sqrt{\{\epsilon/k_B T\}} - 1]\sqrt{\{\pi\epsilon/k_B T\}}) \quad (8)$$

The resulting expression for $k(\epsilon,\theta) \exp(q/k_B T)$ is plotted in Figure 2 as a function of θ for several values of $\epsilon/k_B T$, where the peak values have been normalized to unity. This plot shows, not unexpectedly, that the trajectories of emitted molecules cluster closer and closer around the normal to the surface as the amount of energy in the critical coordinate is increased.

Angular Dependence of Sticking Coefficients

We distinguish between the sticking coefficient, here labeled α, for adsorption onto the liquid surface, and the accommodation coefficient, also commonly labeled α, for transfer from the gas phase via the adsorbed state into the bulk liquid. The present analysis applies to the limiting case of specular reflection from the surface, which in effect means the limit of high kinetic energy. At high energy the structures of the individual molecules that comprise the surface layer and the incident beam are not very important. Every collision is likely to result in immediate contact with the repulsive wall of the interaction potential and

Figure 2. Variation of emission intensity with angle for different values of of $\epsilon/k_B T$, where ϵ is the kinetic energy of the escaping molecule, where all curves have been normalized to a peak intensity of 1.

Figure 3. Fluxes involved in the calculation of the sticking coefficient $\alpha(\theta)$ for molecules leaving a liquid surface at an angle θ to the mean normal and assuming specular reflection. $\tan \theta_N$ is the instantaneous slope of the surface in the presence of thermally excited capillary waves.

so to produce quasi-elastic, near-specular reflection. At low collision energy, on the other hand, a significant fraction of the total kinetic energy is able to be dissipated by interactions between individual structural moieties, leading to a higher sticking probability and making specular reflection much less likely. The effect of diffuse reflection, like the effect of having the surface of the liquid roughened by capillary waves, will tend to average out the angular dependence of the sticking coefficient.

The diagram in Figure 3 shows velocity vectors corresponding to molecules traveling from an arbitrary small volume in the gas to be incident upon the liquid surface at an angle θ to the mean normal, molecules traveling in the opposite direction after being reflected from the liquid surface at an angle θ to the mean normal, and molecules emitted from the surface along the same trajectory. Our basic assumption here is that molecules emitted at the same angle from adjacent elements of gas volume or liquid surface can be regarded as forming a collimated beam and that at equilibrium the flux in such a beam must be the same in both directions. The assumption is a plausible one, which nevertheless needs to be tested by experiment. The angle θ_N in Figure 3 is the deviation of the normal to the local surface from the mean normal as a result of random thermal motion of the surface, i.e., of the presence of many superimposed capillary waves. The reflected molecules are incident at an angle $\theta - 2\theta_N$ to the mean normal and an angle $\theta - \theta_N$ to the local normal, and the emitted molecules are emitted at an angle $\theta - \theta_N$ to the local normal, where both $\theta - 2\theta_N$ and $\theta - \theta_N$ are required to have absolute values less than $\pi/2$. From Table 1, the intensity of the incident beam is

$$I(E,\theta)_{gas,1} = [n_\nu cE\cos(\theta - 2\theta_N)/2k_B^2T^2]\exp(-E/k_BT)$$

$$= I_{gas}\cos(\theta - 2\theta_N) \quad (9)$$

The stream of molecules leaving the surface at the angle θ to the mean normal includes the evaporation intensity given by

$$I(E,\theta)_{liquid} = (3n_sE\cos^2(\theta - \theta_N)/hk_BT)\exp(-[E + q]/k_BT)$$

$$= I_{liq}\cos^2(\theta - \theta_N) \quad (10)$$

where, as shown in Figure 3, $\theta - \theta_N$ is the angle of emission with respect to the local normal. The intensity of the beam reflected from the surface at this angle is given by expression 9, multiplied by a factor $[1 - \alpha(\theta - \theta_N)]$, where in general α is a function of both θ and E and all quantities are to be averaged over the thermal distribution of θ_N. At equilibrium, the sum of these two streams must be balanced by an equal number of molecules moving in the opposite direction, with intensity given by

$$I(E,\theta)_{gas,2} = (n_\nu cE\cos(\theta)/2k_B^2T^2)\exp(-E/k_BT)$$

$$= I_{gas}\cos\theta \quad (11)$$

Hence we obtain

$$0 =$$
$$\beta\cos^2(\theta - \theta_N) + [1 - \alpha(\theta - \theta_N)]\cos(\theta - 2\theta_N) - \cos\theta \quad (12)$$

where $\beta = I_{liq}/I_{gas}$.

At equilibrium we must have a balance between the total absorption and the total emission. Hence

$$\int_0^{\pi/2} I_{gas}\langle\alpha(\theta - \theta_N)\rangle\cos\theta\sin\theta\,d\theta =$$
$$\int_0^{\pi/2} I_{liq}\langle\cos^2(\theta - \theta_N)\rangle\sin\theta\,d\theta \quad (13)$$

where the symbol $\langle x\rangle$ stands for the thermal average of x over θ_N and the integral on the left-hand side cannot be evaluated simply without assuming a functional dependence of α on θ. We choose the form

$$\alpha(\theta) \equiv \langle\alpha(\theta - \theta_N)\rangle = \alpha_0 + \alpha_2\langle(\theta - \theta_N)^2\rangle + \dots \quad (14)$$

When θ is zero, this reduces to

$$\alpha(0) \equiv \langle\alpha(\theta_N)\rangle = \alpha_0 + \alpha_2\langle(\theta_N)^2\rangle + \dots \quad (15)$$

where $\alpha(0)$ is a specified value of the sticking coefficient at normal incidence. From eq 13 we find

$$\beta = (\alpha_0/2 + \alpha_2S_2)/S_1 \quad (16)$$

where S_1 is the integral on the right-hand side of (13), less the factor I_{liq}, and S_2 is the integral on the left-hand side, less the factor I_{gas} and with $<\alpha(\theta - \theta_N)>$ replaced by $<\theta - \theta_N)^2>$. Hence we obtain the following expression for α_2:

$$\alpha_2 = -\{\alpha(0)\langle\cos^2(\theta - \theta_N)\rangle/2 + S_1[(1 - \alpha(0))\langle\cos(\theta -$$
$$2\theta_N)\rangle - \cos\theta]\}/\{(S_2 - \langle\theta_N^2\rangle/2)\langle\cos^2(\theta - \theta_N)\rangle +$$
$$S_1[\langle\theta_N^2\rangle\langle\cos(\theta - 2\theta_N)\rangle - \langle(\theta - \theta_N)^2\cos(\theta - 2\theta_N)\rangle]\} \quad (17)$$

which can be evaluated for any value of θ provided $\alpha(0)$ has

been specified and the distribution over θ_N is known. Since α_2 is supposed to be independent of θ, the problem is now over-determined as a result of our having assumed that eq 14 applies. In practice, on the grounds that the next term in (14) will involve $<(\theta - \theta_N)^4>$ and we require this to be negligible, we take the mean value of α_2 over the range of θ below $\theta^2 = 0.1$, and then use (15) to obtain α_0, after which (14) is used to calculate $\alpha(\theta)$ over the whole range of θ. In principle, there is no difficulty in extending the series (14) to higher terms, but that is not necessary for our present purposes, which are first to check that the theory is capable of giving results in agreement with experiment, and then to compare the results obtained with the $\cos^2(\theta - \theta_N)$ and $\cos(\theta - \theta_N)$ distributions.

The average slope of the liquid surface is zero, so the variance of the slope is equal to the mean-square value. As in our previous calculation of the rate at which a surface molecule is engulfed by the liquid,[16] we can apply the central limit theorem of statistics to obtain the result that the distribution over any function of θ_N is a Gaussian with variance equal to N_m times the variance for a single mode. Here N_m is the total number of vertical modes and is set equal to the total number of molecules in a correlated area of surface, where the size of the correlated area will cancel from the final result. The details of the derivation are as follows.

For a capillary-wave mode of the form

$$\zeta = a\sin(\omega t - kx) \quad (18)$$

where ζ is the vertical displacement of the surface, the energy per unit area is $a^2k^2\gamma/2$,[25] where γ is the surface tension and k is the wave vector along the x axis. If the (macroscopic) correlated area of surface has diameter L, the corresponding area is $\pi L^2/4$ and the energy per mode becomes $\pi L^2a^2k^2\gamma/8$. The number of modes is $\pi L^2/4\sigma^2$, where σ is the molecular diameter of the solvent, the average energy per mode can be equated to k_BT, and the mean-square slope ζ'^2 of one mode, averaged over a whole number of wavelengths, is $a^2k^2/2$. Hence, after taking notice of the fact that the contributions to ζ'^2 from the x and y modes are equal, the (un-normalized) distribution of slopes is given by

$$P(\zeta') = \exp(-\zeta'^2\sigma^2\gamma/2k_BT) \quad (19)$$

where ζ' is $\tan\theta_N$. To use this result, we first set up a grid of evenly spaced values of $\tan\theta_N$ in the interval $-\pi/2$ to $\pi/2$ and normalize $P(\zeta')$ so that its sum is unity. A grid of evenly spaced θ values is then set up over the range 0 to $\pi/2$, the various thermal averages of eq 17 are calculated for each value of θ, and the integrals S_1 and S_2 are evaluated by Simpson's rule. The sticking coefficient $\alpha(\theta)$ is then evaluated for a series of specified values of $\alpha(0)$, as outlined above. For the purpose of comparison, the calculations are also carried out with $\cos(\theta - \theta_N)$ factors in place of the $\cos^2(\theta - \theta_N)$ factors in eq 17. A Fortran listing of the computer program is available from phillips@chem.canterbury.ac.nz.

Fiehrer and Nathanson[26] have measured sticking coefficients as a function of kinetic energy and angle for a variety of different molecules impinging on the surface of concentrated (azeotropic) sulfuric acid at 295 K, with values of $\alpha(0)$ ranging from about 0.4 to near unity. Their results, which are plotted in Figure 4, show that $\alpha(\theta)$ decreases with increasing kinetic energy and with increasing θ, the angular dependence being more pronounced at higher energy. The observed slight dependence of the degree of curvature on the nature of the impinging gas possibly implies the existence of interesting differences in the amount of specular reflection between different molecules.
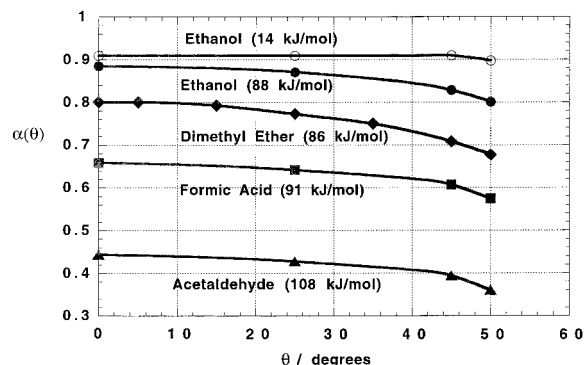
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Figure 4. Experimental dependence of sticking coefficients on 98.8 wt % sulfuric acid, as measured by Fiehrer and Nathanson.[26] The incident beam energy is given in parentheses for each substance.
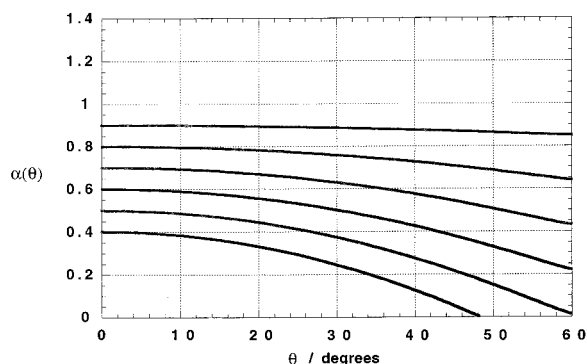

Figure 5. Calculated sticking coefficients with emission intensity proportional to $\cos^2(\theta - \theta_N)$.

A difficulty that arises in making calculations for this surface is that the best value to use for the molecular diameter σ is not immediately obvious with a structured and highly associated liquid such as sulfuric acid.[27] In the present model this quantity is important because it controls the number of capillary-wave modes in a given area of surface, and the shortest-wavelength modes actually have $\lambda = 2\sigma$. The model was constructed for a liquid composed of weakly interacting spheres, and with a liquid as complex as concentrated sulfuric acid, it can be expected to break down for wavelengths close to molecular dimensions. The quantity σ therefore has to be regarded as an adjustable parameter, whose value is to be chosen so as to mimic the average behavior of the real system by one composed of noninteracting spheres, and it is not necessary for σ to be equal to the true molecular diameter of the molecules comprising the liquid. Nevertheless, it is reasonable to expect that σ should not differ from the actual molecular diameter by more than 1 order of magnitude, and in the present calculations, this will provide us with a means of discriminating between the distributions with $\cos^2(\theta + \theta_N)$ and $\cos(\theta + \theta_N)$ angular dependence.

Our results for this liquid surface are shown in Figure 5 for $\alpha(0)$ in the range 0.4−0.9, where we have used $\sigma = 1.2 \times 10^{-7}$ cm. These results are in good qualitative agreement with the experimental data obtained by Fiehrer and Nathanson at high collision energies. The numerical effect of increasing σ is to cause the falloff of α with increasing θ to be more pronounced, and higher values of σ are required to reproduce the observed falloff at higher values of $\alpha(0)$. For $\alpha(0)$ below 0.7, acceptable results are obtained with $\sigma = 0.6 \times 10^{-7}$ cm. The results in Figure 6 for $\alpha(0)$ in the range 0.4−0.9, with $\sigma = 1.2 \times 10^{-7}$ cm, were obtained after the $\cos^2(\theta + \theta_N)$ factors in eq 17 had been replaced by factors $\cos(\theta + \theta_N)$, in accordance with the Maxwell distribution of eq 3. The upper three curves in Figure
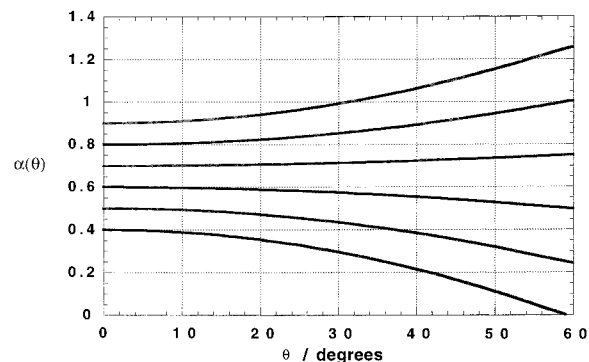

Figure 6. Calculated sticking coefficients with emission intensity proportional to $\cos(\theta - \theta_N)$.

6 clearly do not conform with the experimental data, which always shows α decreasing with increasing θ, and they cannot be made to conform with experiment, even with unacceptably large values of σ. For example, for $\alpha(0) = 0.9$, the value of α at 60° is 1.258 with $\sigma = 1.2 \times 10^{-7}$ cm (plotted in Figure 6), 1.186 with $\sigma = 2.4 \times 10^{-7}$ cm, and 1.172 with $\sigma = 3.6 \times 10^{-7}$ cm. Thus the experimental data can be regarded both as supporting the theory behind eq 17 and favoring the distribution with $\cos^2(\theta - \theta_N)$.

The observed angular dependence of the desorption coefficient for molecules leaving a solid surface[18] is not dissimilar to the dependence found by Fiehrer and Nathanson for molecules striking a liquid surface, which implies that there may be some useful correspondences between the equilibrium distribution of surface irregularities on a solid and the departures from planarity of a liquid surface in the presence of thermally excited capillary waves. This might be regarded as the converse of the statement that, from the viewpoint of an incoming molecule at moderately high collision energy, the surface of a liquid appears as a frozen landscape.

Conclusions

Of the three forms of Maxwell distribution that have been employed for the molecules evaporating from a liquid surface, the best one to use is the distribution for effusion through a small hole, as given in eq 3 and as generally used by workers in the field of gas−solid interactions. However, whenever the angular dependence of emission is important, the form derived from statistical reaction-rate theory, with a $\cos^2 \theta$ factor, should be used instead. Also, when the angular dependence is important, allowance must be made for the presence of a statistical distribution of surface irregularities in the case of a solid, and of capillary waves in the case of a liquid. The available experimental evidence in the form of measured velocity distributions is insufficient to discriminate between the distribution of eq 3 and "floating" distributions of the form of eq 2. The discrimination between the distribution (3) and the distribution derived from statistical reaction-rate theory, on the basis of the measured angular dependence of sticking coefficients, is clearly in favor of the latter form with its cosine-squared factor.

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