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Molecular Scattering at the Solid Surface

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I. Introduction

From the days of its first development the molecular beam has been recognized as a powerful tool in the study of gas-surface interactions. Such investigations in great measure were stimulated and given momentum by the early work of Stern and his associates. This classic period was climaxed, although by no means terminated, by the work of Estermann and Stern[1] in studies of the diffraction of helium atoms and hydrogen molecules at surfaces of cleaved crystals. Within recent times, and concurrent with the considerable advances made in the kinetic theory as applied to the mechanics of rarefied gases, interest in the physics of interaction at the gas-surface interface has become renewed and the molecular beam has once again been applied to the study of these problems. For the most part these studies have been undertaken with the broad objective of supplying the microscopic detail of momentum and energy exchange between the directed particle and the surface. The present paper describes a series of such studies recently undertaken at the University of California,* and discusses the consequences of the findings to fluid friction in a rarefied gas flow.

II. Experimental

The work was conducted in an apparatus resembling, in much of the external detail, one of the more conventional atomic beam equipments. The essentials of the system are indicated in Figs. 1a and 1b. In addition to the elements illustrated, the equipment contained many of the familiar components of vacuum technology, oil vapor diffusion pumps, refrigerated traps, monitoring gages, and a gas supply system. The axi-symmetric configuration of Fig. 1a was chosen to permit observations of the scattered molecule flux at any position on the

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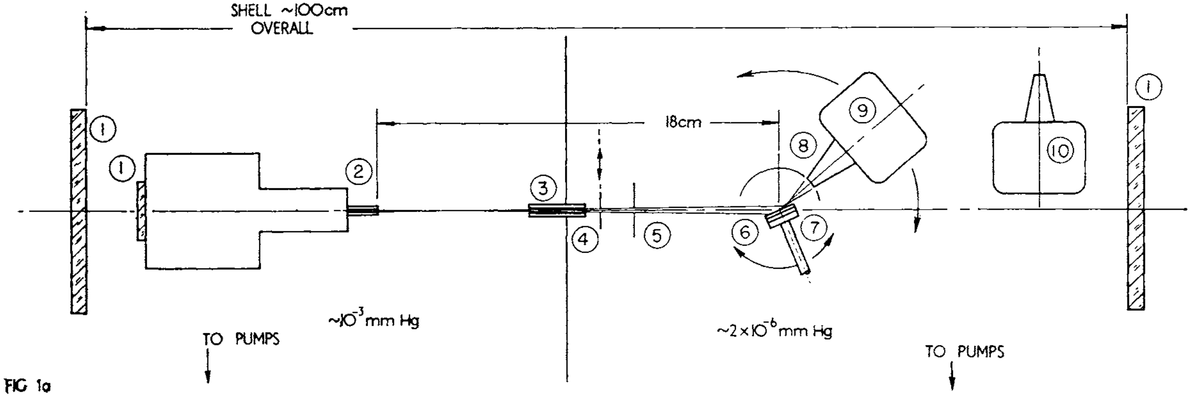


FIG 1a

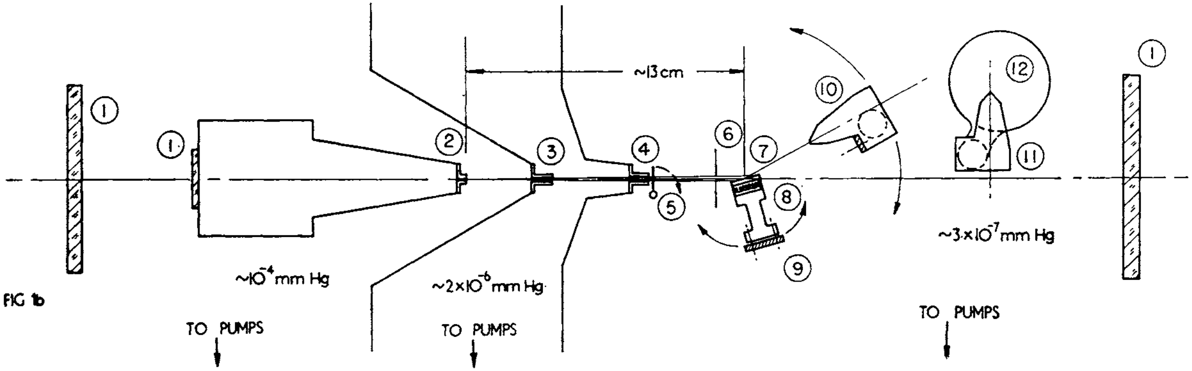
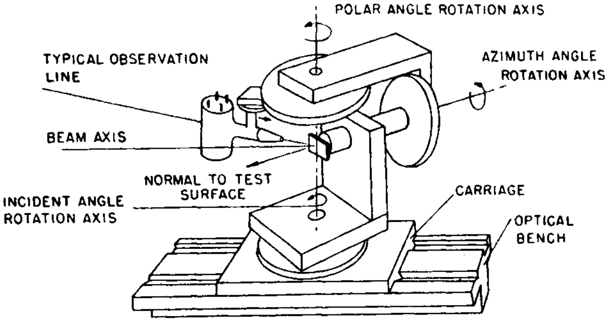


FIG 1b

Fig. 1a. Beam apparatus schematic—axi-symmetric geometry: (1) window for beam alignment, (2) source tube, (3) defining tube, (4) shutter, (5) secondary defining orifice, (6) specimen surface, (7) support pedestal, (8) detector entrance cone, (9) detector gage, (10) comparator gage and cone.

Fig. 1b. Beam apparatus schematic—two-dimensional geometry: (1) window, (2) source channel, (3) fore channel, (4) defining channel, (5) shutter, (6) secondary defining slit, (7) specimen surface, (8) heater, (9) support pedestal, (10) detector head, (11) comparator head, (12) comparator gage.

available hemisphere including, therefore, observations at positions out of the incident plane. The angular aperture of the detector was fixed at 0.005 steradians by considerations of the minimum resolvable signal, the cone angle being therefore approximately 0.3 radians. The source was unheated, and no fore-slit was employed, the necessary pressure ratios between regions being maintained by long defining tubes of low conductance. In the test region the target specimen was supported in such a way as to provide arbitrary orientation of specimen and detector with respect to the incident beam (Fig. 2). Immediately preceding the target specimen was fixed a thin-edged orifice serving as a final stop in the geometrical definition of the beam.

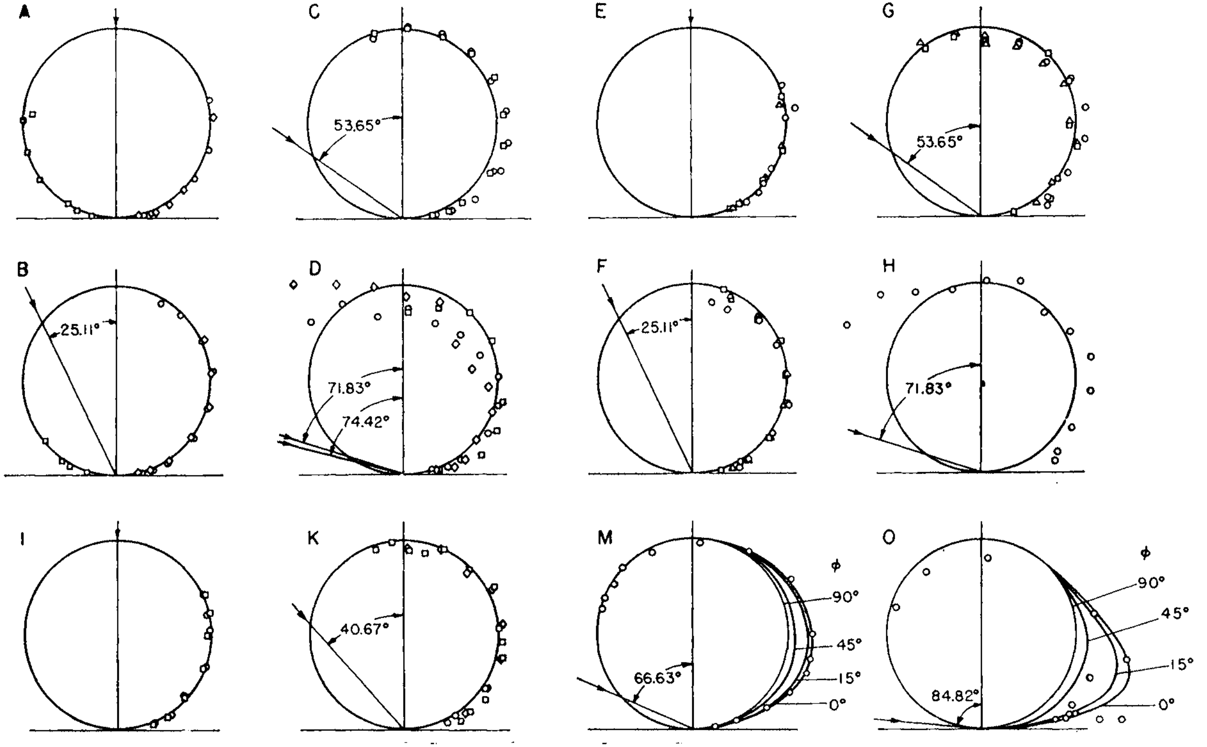


SCHEMATIC OF BASIC ROTATION ELEMENTS OF DETECTOR MECHANISM

Fig. 2

The two-dimensional geometry, Fig. 1b, was employed in the most recent studies in order to permit the performance of a higher resolution experiment, particularly in respect to measurement near glancing incidence. It was found to be desirable in this case to introduce the region of differential pumping illustrated, and to make certain refinements in the pumping and trapping system. It was found possible to reduce the plane angle subtended by the detector slit to 0.01 radians.

The ionization gage was selected for development as the molecular beam detector in this apparatus because of its high sensitivity and its relative freedom from thermal instabilities. As in the more familiar Pirani detection system, the measurement cycle is initiated by withdrawal of the shutter, the beam strikes the target and scattered molecules fill the reservoir of the gage. Also, as in the Pirani system, a comparator gage performs the necessary background pressure measurement. The problem in such a system lies in the maintenance of


A
C
53.65°
E
G
53.65°
B
25.11°
D
71.83°
74.42°
F
25.11°
H
71.83°
I
K
40.67°
M
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90°
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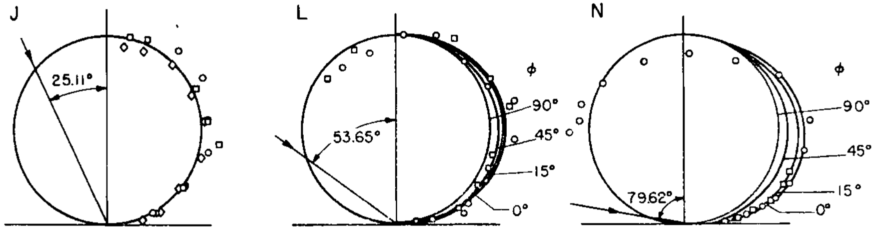

Fig. 3. Polar plots of the scattering data—axi-symmetric geometry.

Plot	Surface	Incident angle	Azimuth angle	Symbol	Date
A	Polished steel	0.00°	0.00°	○	2-15-53
		0.00°	0.00°	□	2-17-53
		0.00°	19.57°	◇	2-21-53
B	Polished steel	25.11°	0.00°	○	2-15-53
		25.11°	0.00°	□	2-17-53
		25.11°	19.57°	◇	2-21-53
C	Polished steel	53.65°	15.94°	□	2-26-53
		53.65°	0.00°	○	2.27-53
D	Polished steel	71.83°	15.94°	◇	2-26-53
		74.42°	15.94°	□	2-24-53
		71.83°	0.00°	○	2-27-53
E	Polished aluminum				
	unheated	0.00°	0.00°	○	3-23-53
	heated	0.00°	0.00°	□	4- 7-53
	unheated	0.00°	0.00°	△	4- 8-53
F	Polished aluminum				
	unheated	25.11°	0.00°	○	3-23-53
	heated	25.11°	0.00°	□	4- 7-53
	unheated	25.11°	0.00°	△	4- 8-53

Plot	Surface	Incident angle	Azimuth angle	Symbol	Date
G	Polished aluminum				
	unheated	53.65°	0.00°	○	3-23-53
	heated	53.65°	0.00°	□	4- 7-53
	unheated	53.65°	0.00°	△	4- 8-53
H	Polished aluminum				
	unheated	71.83°	0.00°	○	3-23-53
I	Unpolished glass	0.00°	0.00°	□	5-16-53
		0.00°	19.57°	○	5-23-53
J	Unpolished glass	25.11°	0.00°	○	5-16-53
		25.11°	0.00°	◇	5- 5-53
		25.11°	19.57°	□	5-17-53
K	Unpolished glass	40.67°	0.00°	○	5-16-53
		40.67°	15.58°	□	5-23-53
		40.67°	35.83°	◇	5-25-53
L	Unpolished glass	53.65°	0.00°	○	5-16-53
		53.65°	0.00°	□	6-18-53
M	Unpolished glass	66.63°	0.00°	○	6-20-53
N	Unpolished glass	79.62°	0.00°	○	6-21-53
		79.62°	15.58°	□	5-23-53
O	Unpolished glass	84.82°	0.00°	○	6-21-53

sufficiently stable electron emission at the ionization gage cathode. For the purpose of these studies emission regulators and a difference detector* were developed which permitted resolution of signals to less than 10^{-10} mm Hg in the presence of fluctuations in the background pressures of the order of 10^{-8} mm Hg. In the case of the axi-symmetric system with a path length of the order of 18 cm, background pressure within the beam chamber was approximately 2×10^{-6} mm Hg, and the maximum pressure increments within the gage due to the influx of the scattered beam were of the order of 10^{-9} mm Hg. In the two-dimensional configuration with a somewhat shorter path length and higher resolution detector geometry, the scattered beam pressure increments are of the same order in the presence of background pressures of the order of 3×10^{-7} mm Hg.

The first sequence of studies was performed with the axi-symmetric geometry employing beams of nitrogen and surfaces of cold rolled steel and of aluminum prepared by conventional metallurgical polishing. Similar surfaces polished and then etched in the conventional manner, and surfaces of common window glass both "as cooled" and optically polished were also used. Precautions were taken to insure cleanliness of the test surfaces within the limitations imposed by the apparatus. The metal surfaces were heated in some instances, but were not consistently degassed, nor were they held at elevated temperature for all traverses. The glass surfaces were not heated in the course of these experiments. Polar representations of the data are presented in Fig. 3, and dates and descriptive material relative to the plots appear in the caption below.

The ambiguities stemming from the non-uniformity of surface history were in part removed in the two-dimensional studies by the use of a small radiant heater mounted just beneath the surface within the support pedestal. By means of this heater it was possible to degas the surface before each run and then maintain it at approximately 100° C for the balance of the running period. Polished glass and Teflon were used as the target specimens, while air, nitrogen and argon were used as the beam gas. Only the glass surface was degassed in this series. Representative polar plots of the experimental results are presented in Fig. 4.

III. Discussion

An inspection of the polar representations of the data reveals the salient feature of the findings; by far the greatest number of molecules are scattered at random, as from an ideally rough surface, for all

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* An Ionization Detection System for Molecular Beams. (To be published.)

combinations of gas and surface. The measured flux distributions adhere closely to the cosine or "diffuse" scattering pattern and show no sharp perturbation of that pattern; no "specular" lobes are observed. On the other hand, there is in evidence a small, although measurable, departure from cosine scattering in the cases of the glass and Teflon surfaces. In these cases, and the data of 1957 for glass repeated that of 1953 in this respect, a small fraction of the incident molecules was scattered into directions lying about the specular ray in addition to that expected on the basis of a purely random distribution. Furthermore, in the case of the glass surfaces it would appear that the fraction so scattered increased with increasing angle of incidence, although to the limiting angle of the experiment, about 89.5° in the more recent case, no evidence was obtained of a sharper form of specular scattering.

There is a substantial resemblance between these data and those of Zahl[2] and Josephy,[3] obtained in studies of the scattering of Hg from cleaved NaCl crystals. The specular fraction in these cases, however, was of much greater magnitude than the diffuse. Zahl reported complete diffuse scattering of Hg from glass. A point of distinction between the data of Zahl and those of the present studies with glass is found in the constancy of the amplitude of the specular lobe in Zahl's case at all incident angles even near normal incidence. On the other hand, it is just here that the observations of scattering from the Teflon surface may be found to differ from those involving glass. An inspection of Fig. 4 reveals a distortion of the cosine distribution in the Teflon studies which persists to substantially smaller angles of incidence than in the other case.

It is difficult on the basis of the present observations to go far toward the formulation of theories of interaction or even toward the precise characterization of the surface itself. It would seem likely that the best language with which to discuss these matters remains for the present that of classical physics. In these terms it would appear that the surface is rough on a molecular scale, a not unexpected conclusion. It is known from studies of energy accommodation at surfaces[4] that the adjustment in energy is much less completely accomplished in general than the adjustment of momentum, as may be judged from the present experiment. It has frequently been argued that all interactions are more or less specular, in that they involve a sticking time or time of adsorption at the surface which is short by comparison with the time needed for the adjustment of molecular energy to that of the surface, but that the molecule is trapped in fissures and in the mean makes several collisions with the surface. It may require numerous

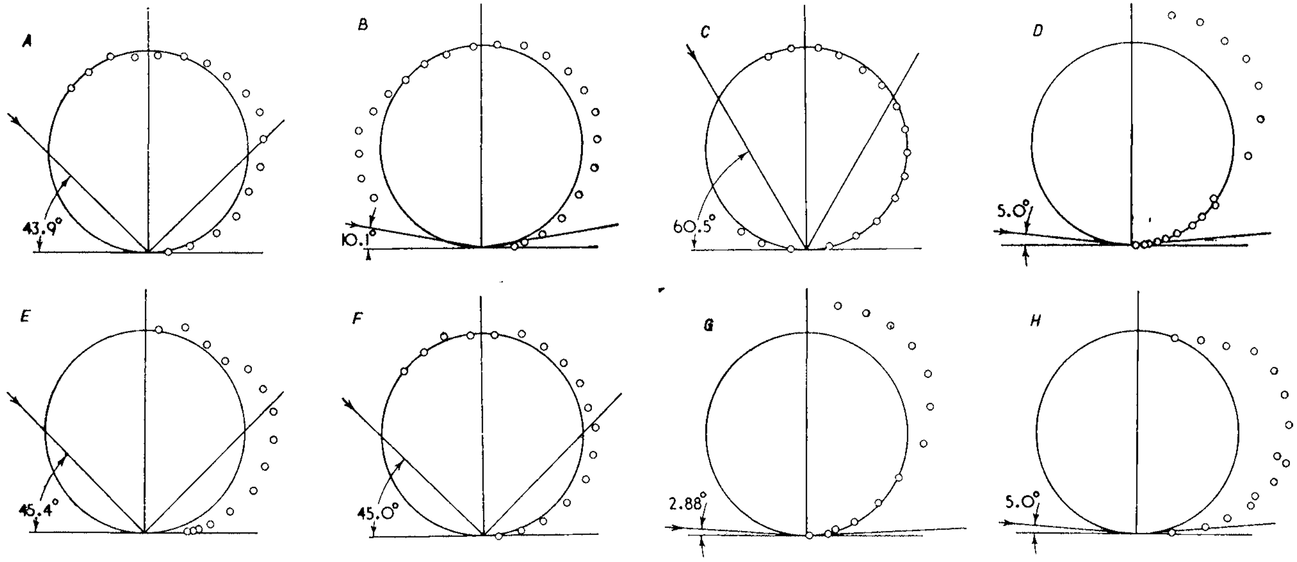
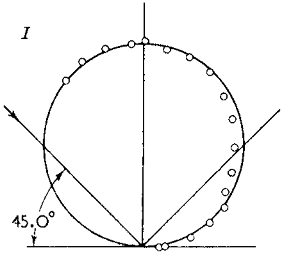


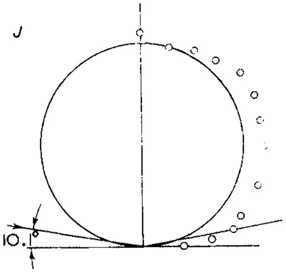
Fig. 4. Polar plots of the scattering data—two-dimensional geometry.

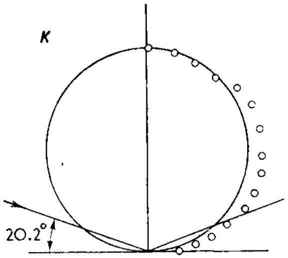
Plot	Gas	Surface	Incident angle	Date
A	N_2	Teflon	43.9°	12-10-57
B	N_2	Teflon	10.1°	12-10-57
C	Argon	Teflon	60.5°	12- 6-57
G	Argon	Teflon	2.88°	11-19-57
E	Argon	Teflon	45.4°	11-21-57
F	Argon	Teflon	45.0°	12- 6-57
D	Argon	Teflon	5.0°	11-19-57
H	Argon	Polished glass	5.0°	11- 7-57

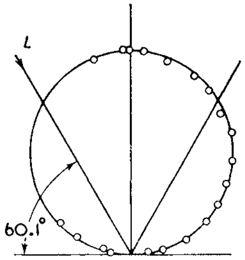
L

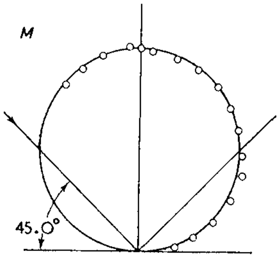
I	Argon	Polished glass	45.0°	9- 6-57
J	Argon	Polished glass	10.1°	9- 5-57
K	Argon	Polished glass	20.2°	9- 5-57
L	Air	Polished glass	60.1°	8- 1-57
M	Air	Polished glass	45.0°	8- 1-57
N	Air	Polished glass	10.1°	7-31-57
O	Air	Polished glass	20.1°	7-31-57

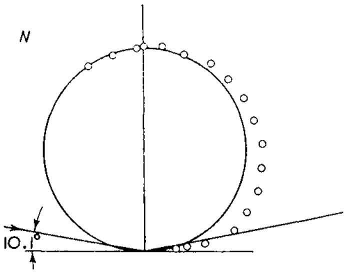


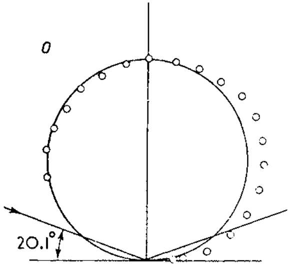












collisions, in that view, to accomplish a complete adjustment in energy, but only one or two to accomplish the observed loss of influence of the incident trajectory. Such an argument has a certain plausibility in the case of reasonably clean and degassed surfaces as in the second sequence of experiments reported here, although it would not be expected to apply in the case of single crystal surfaces. These remarks have been made at this length only in order to make plain that the present studies shed no light on the details of energy accommodation at the surface. Both the "specular" and the "diffuse" interactions may have occurred without energy exchange, or equally well with some adjustment in energy toward that of a gas at the surface temperature.

It is interesting to consider to what extent the above difficulty may be resolved by the examination of experiment in the field of rarefied gas flow and to obtain in this process some understanding of the consequences of these results to fluid friction in such flows. Two gas-surface interaction parameters are commonly employed in the formulation of boundary conditions for rarefied gas flows and are discussed in textbooks on kinetic theory as the coefficient of momentum transfer, f (coefficient of specular reflection), and the coefficient of energy accommodation, α. It is with the first of these coefficients that we shall be concerned here. This coefficient was proposed by Maxwell and discussed in terms of a fraction $1-f$ of molecules specularly reflected in interaction with the surface, and a fraction f diffusely reflected. In a near equilibrium flow of a gas past a surface one may identify the quantity f defined in this manner with f defined as that fraction of the incident tangential momentum which is transferred to the surface in the momentum exchange. We may write

$$f = \frac{G_i - G_r}{G_i} \tag{1}$$

in which G_i is the magnitude of the tangential momentum brought to the surface by all incident molecules, and G_r is that which is transferred to the issuing molecules by the surface. Conservation in molecular number density at the surface is assumed.

It has been shown[5] in the case of a rarefied gas in laminar flow parallel to a surface that one may calculate the value of f in accordance with Eq. (1) where the interaction details necessary to the calculation of G_r are supplied from molecular beam experiment. In order to complete the calculation where only information relating to the angular distributions in the scattered flux is available from experiment, assumptions must be made relating to the nature of the exchange of energy at the surface. Two limiting assumptions are available: (1) that the specular component, i.e. those molecules appearing in the specular lobe in excess of the number expected on the basis of diffuse scattering, is completely adjusted in energy to that of a gas in equilibrium at the temperature of the surface, and (2), that the specular component is totally unadjusted in energy and retains in consequence the energy of its initial trajectory. One may then characterize the assumed rarefied gas flow of this calculation by means of s, the molecular speed ratio, where

$$s = \frac{U}{V_m} \tag{2}$$

where U is the mass velocity of the gas flow and V_m is the most probable thermal speed of the molecules. It can be seen that as U becomes large with respect to V_m a predominance of momentum will be incident on the surface at angles close to glancing. Where the flux of molecules comprising the specular component is in part a function of the angle of incidence of the molecule on the surface, one can see that the calculated value of f will in general be a function of the parameter s. Calculations on the basis of both extremal assumptions for the case of the nitrogen-glass interaction have been carried out and the results are presented in Fig. 5.

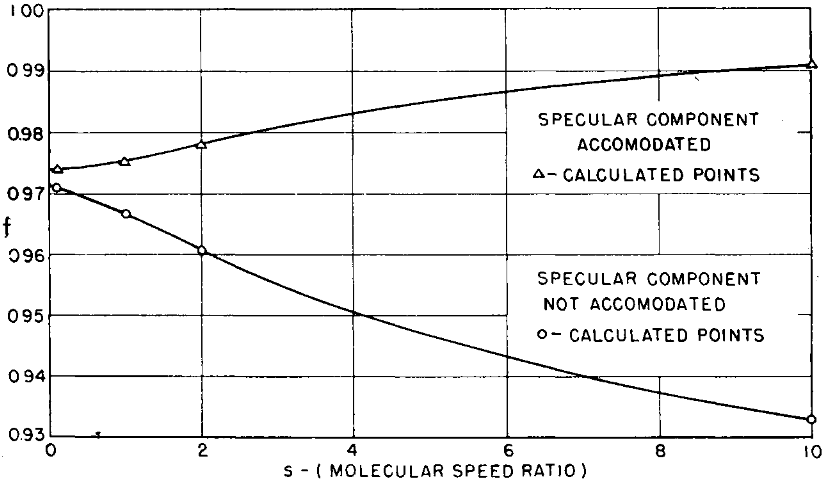


Fig. 5

It is seen that as the relative speed of gas and surface increases the value of f decreases in the case of assumption (2). By means of friction drag studies in rarefied gas flows, as might be performed in a rotating cylinder apparatus one might well determine which of the limiting assumptions lies closer to reality, provided adequate surface cleanliness could be assured and suitable values of s achieved. A somewhat more immediate result of this calculation lies in the realization that very large and readily discernable lobes would be required if calculated values of f substantially below 1 were to result. Thus, calculations of aerodynamic forces on bodies in rarefied atmospheres which have been made on the assumption that f can be taken as unity for practical purposes can be seen to rest on a reasonable experimental footing. One should guard very carefully, however, against an uncritical extrapolation of these results for low interaction energies to calculations involving interaction energies of the order of 1 to 10 electron volts. Much work must yet be done before sufficient experience has been gained either for the formulation of theories of the interaction or even for gas mechanic prediction where the interaction energies of particle and surface are high.

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