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RESEARCH ON GAS-SURFACE INTERACTIONS 1966-67

PART I - PROJECT SUMMARY

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PART I – PROJECT SUMMARY

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INTRODUCTION AND SUMMARY

This report presents a summary of the research on gas-surface interactions conducted during the period 11 August 1966 through 11 October 1967 under Contract NASw-1461. Previous work in this area has been reported in Refs. 1 through 9. A separate but closely related research project supported under Contract NAS 8-21090 is reported in Ref.10, exploring the feasibility of conducting gas-surface interaction experiments in a satellite.

The major portion of the theoretical work under this contract is described in Part II of this report, RE-306. Herein we discuss several other aspects of the theoretical research, and describe the experimental work.

The experimental program included research on a high intensity shock tube driven molecular beam for use in surface interaction experiments and the development of two separate methods for preparing and analyzing surfaces for targets in these experiments.

THEORETICAL PROGRAM

Most of the theoretical effort during this contract has been on the application of our computer methods to the scattering of noble gases from single crystal silver surfaces, as described in detail in Part II of this final report. We chose to emphasize that part of the effort because it offered the possibility of a meaningful test of the theory, and because an idea for extracting spatial distributions from reasonable numbers of trajectories showed promise. The results of this effort show enough agreement to be encouraging, and have pointed the way to weak points that need further work in both theory and experiment.

The rest of our theoretical effort has been done in two basic areas. The first was an attempt to develop an analytical scattering theory to predict (before trajectory computation or experimental measurement) the spatial distributions of flux and other important properties; the second marked the beginning of an effort to study recombination of atomic species at a surface. The scattering theory work was closely related to that described in Part II and to the work of Erofeev (Ref.11). If it continues to show promise, the recombination study will comprise a significant portion of our effort over the next year.

Analytical Scattering Model

The need is still evident for an analytical scattering model to be used with numerical scattering results. Starting with the theory of Erofeev (Ref. 11), we programmed the numerical evaluation of his equations for flux, adding simple corrections to allow the size of the target atoms to change with incident energy and to give first-order effects of lattice restraining forces. The results for several cases appear generally similar to those Erofeev reported,

and fail to show the degree of sharpness or the multiple peaks that we and others (e.g., Ref. 12) have found. We believe that a more detailed representation of the lattice surface geometry will be required to show the indicated behavior, which is disappointing in view of the mathematical complexity of Erofeev's model.

The difficulty appears to be that while Erofeev calculates the fraction shadowed and subtracts it from the differential cross section, he does not take into account the nonuniformity of the shadowing effect. For example, the particles scattered near the specular direction and closer to the surface tend to come from glancing collisions, and shadowing corrections to the local differential scattering cross sections should be quite small in these regions. Backscattered particles, on the other hand, come from collisions that are closer to lines of centers and these regions of the surface are quite apt to be occluded by other surface atoms. Unfortunately there does not appear to be a straightforward way to describe these effects in terms of the geometry of a real surface.

Atomic Recombination at a Surface

It has been demonstrated repeatedly in our own work (e.g., Ref. 5) and in that of many others (e.g., Ref. 13) that adsorbed contaminants can have a very significant effect on gas-surface interaction. We find that the largest unknown in the prediction of aerodynamic drags and torques, particularly under orbital conditions, lies in the surface condition.

If the surface is clean, we can expect an interaction that will give moderately broad, generally specularly directed, scattering in which the capture of incident particles is limited to

atoms of oxygen with about a 0.30 sticking probability. The energy exchange of the remaining components would follow the familiar hard sphere law, with corrections of the type given in Ref. 3. To reduce drag, heavy atomic weights in the surface (and high Debye temperature in some cases) would be helpful for surfaces at low inclination to the free stream or facing aft and for light atoms facing forward. But for most cases we do not expect the surface to be clean. It may be launched dirty, in which case time and the space environment can be expected to produce a continuous change in gas-surface interaction as the surface loses species in the order of increasing binding energy. This case must be analyzed by ad hoc methods. A more difficult problem arises when we study the steady state case of space exposure, in which the crucial question centers upon the relative rates of adsorption and desorption of atomic oxygen.

Of all the species present in high concentration in the 50 - 1000 km region (where aerodynamic effects are most important), the one with the highest probability of sticking to a surface is O. Since one O atom is bound to another with a high binding energy and forms a roughly equivalent bond with many possible surface atoms, the possibility of an important desorption mechanism lies in the O - O recombination. The energy released by the formation of O_2 may or may not become available to desorb the product molecule, which should have a much lower binding energy with most metallic oxides. If such a process is not likely, the surface will become covered with O in a very short time. If it is likely, the surface coverage will be very low.

Because we believe this associative desorption might become one of the most important questions in gas-surface interaction,

and since it is related to possible future extensions into the area of surface catalysis, we have begun to study this process with our computer models. The principal difficulty is the primitive state of our knowledge of interatomic potentials. If we can construct a consistent model for the potential surfaces of three mutually interfering atoms, the computation of representative interactions at the satellite energy level will not present any new problems. For the results not to be misleading, however, we must be able to treat several rather different potential models and display the expected reaction mechanics for each. Confidence in the final outcome will depend greatly on how sensitive the results are to details of the potential surfaces. This is quite different from the problems we have treated thus far, in which only the gross features of the potentials have had important effects on the results.

About one-half the programming for this new phase of our work has been completed. A considerable amount of study of various potential surface models has been done, but a great deal more will be required in the coming year.

MOLECULAR BEAM SYSTEM

A shock tube driven molecular beam system has been developed for the experimental study of gas-surface interactions in the epithermal range. A complete description of the apparatus is given in Ref. 6. During this contract we have prepared the molecular beam system and associated instrumentation for gas-surface interaction experiments on vapor deposited silver surfaces. The work has included calibration and installation of an array of eight electron bombardment ionization gauges (through-flow type) for measuring density distributions scattered from a surface; development in our own lab of the Saltsburg-Smith technique for creating epitaxial surfaces by continuous deposition; X-ray diffraction of surfaces so produced to confirm their monocrystalline (111) state; and efforts to improve the beam's reproducibility and determine its performance envelope.

The calibrations of our through-flow detectors indicate that the transducers have sufficient sensitivity (5×10^{-18} amp-molecule^{-1}cm^{3}) and frequency response (15 kHz) for the measurement of reflected beam number density and mean velocity. The problem of reproducibility took longest to solve, and we have not yet determined performance limits. We have produced a satisfactory reproducible N_2 beam with a measured translational energy of 0.4 eV. With the same shock tube conditions Ar should have much higher energy. We find that failure to recover energy from internal degrees of freedom becomes an increasing problem in N_2 since we have to reduce operating pressures in the shock tube to produce faster shocks. Increased vibrational excitation and decreased relaxation rates for all modes conspire to reduce efficiency of conversion to translational energy in the expansion. We have

also found that performance is limited by the size of our shock tube, particularly its inadequate diameter.

Experiments now being performed are designed to maximize the energy and intensity of these beams and to minimize their cold gas entrainment (Ref. 6).

Molecular Beam Density Variations

In the mode of operation we employed until quite recently, the ball valve nozzle at the end of the shock tube is opened just prior to shock arrival. Test gas at room temperature then starts to flow through the nozzle and beam forming elements to produce a thermal energy (.05 eV) molecular beam. The interaction between the high energy flow (after the shock reflects from end wall) and the cold flow yields a high energy beam that has from 75 to 85 percent of the maximum obtainable velocity (based on stagnation enthalpy) and about 5 times higher number density than could be obtained without cold flow. Unfortunately a large variation in intensity and energy levels from one run to another is inherent in this mode of operation. In a previous report (Ref. 9) we expressed the hope that these variations could be eliminated by more careful control of the timing of the nozzle opening relative to the shock arrival. Recent findings eliminate that possibility since the variations continue under the most carefully controlled sequences. Since reproducibility of the flux greatly increases the utility of the beam in a scattering experiment, we have tried to improve it by using a fixed nozzle with a conventional cellophane diaphragm. With the knowledge that this change reduces the variations to an undetectable level (see below), and aided by inference from measurements with electron bombardment ionization gauges, we can deduce that the nozzle starting period extends

through the entire test period for the mode in which the nozzle is open before shock arrival. The analysis of such a starting transient is much more difficult than that of the conventional nozzle starting problem (see Smith, Ref. 14) since the ambient gas is expanding through the nozzle before start. The molecular beam operating in a transient mode does not in itself cause a problem, but the resulting variations require monitoring and correction as successive shots are employed to complete a scattering pattern. We therefore altered our operating mode to eliminate the trouble.

Fixed Nozzle Operation

The cold gas flow was eliminated by fixing the nozzle in the full open position and inserting a cellophane diaphragm near the nozzle throat to maintain vacuum conditions in the test section. Shock arrival at the nozzle location ruptures the diaphragm and thereby initiates a high energy flow that is then collimated in the usual fashion. Several milliseconds later the nozzle is rotated to the closed position to prevent metal diaphragm particles (used to generate the shock) from entering the test chamber and to prevent excessive chamber pressure increase. Although we feared it would erode our skimmers and gauges, we have not encountered adverse effects from the cellophane diaphragm.

We have run extensively in this mode, using both heat transfer gauges (which detect energy flux) and through-flow ionization gauges (which measure local instantaneous density). The results are reproducible, but lead to a reduction in intensity to about 20 percent of the average value for the former rotating nozzle mode. The ionization gauges, which we had never before been able to use successfully in the incident beam, have been operated in a

low voltage mode to reduce breakdown. Although they become highly nonlinear at the high densities, they reveal a very interesting feature of the starting process.

As Smith (Ref. 14) describes the starting process for a fixed nozzle, if all of the expansion from stagnation (Region 5 in shock tube notation) to perfect vacuum takes place unsteadily and at constant area, it produces a limiting velocity of $2a_5/(\gamma - 1)$; the steady expansion value, on the other hand, is $(2/\gamma - 1)^{\frac{1}{2}}a_5$, or about half the unsteady value for $\gamma = 1.4$. The unsteady expansion flow is followed by a steady expansion, but that portion of the fluid that undergoes unsteady expansion has a very much lower final density. We consistently observe on the density gauges a precursor pulse which has a time-of-flight about half that for the steady-flow pulse that follows it. We had never before been able to detect this precursor because of its very low density; the ionization gauges see it easily. Although we cannot accurately determine the density ratio between the precursor and the steady pulses because the density gauge is swamped by the steady pulse, all indications are that the steady pulse is at about the intensity predicted by an inviscid expansion analysis using the method of characteristics. Previous such comparisons with the rotating mode (Ref. 9) gave signal levels that were too high, but were of the correct shape and scaled properly with changes in density and flow area.

Time of Flight Measurements in the Beam

A seven-element heat transfer rake was located in the test chamber with one of its elements on the optical centerline of the system. By maintaining constant shock tube source conditions and recording the heat transfer data at two different locations (with

respect to the collimator), we obtained the mean velocity from which we calculated the number density, assuming the gauge had an accommodation coefficient of unity (i.e., $\rho \approx 2q/u^3$).

Measured beam velocities were 20 to 30 percent lower than ideal (depending on shock tube source pressure), and the calculated number densities were approximately 50 percent lower than measured values obtained by using a single skimmer. Several different source conditions have been considered and the nominal beam number density in the test section is 10^{12} molecules N_2/cc with beam energies up to 0.4 eV/molecule.

These measurements are more accurate than those we made in the past (Ref. 9) because we can now take advantage of the reproducibility of the beam. Previous measurements could only resolve the time difference between shock arrival at the end of the shock tube and beam arrival at the target. We were then forced to assume a constant beam velocity between these events, ignoring starting times and the low velocity region near the nozzle throat. These corrections were noticeable and differed at various energy levels. We get similar results from tandem mounting of ionization gauges, but, as noted above, they become highly nonlinear at the high beam densities we use.

We have adequate test time, which is consistent with predictions using Mirel's interface mixing shock tube theory. That is, test time is limited by shock tube operating conditions; for our tube we expect an upper limit on beam energy of approximately 1 eV/molecule with test time of approximately 0.1 millisecond. Higher beam energy can be obtained by increasing the shock tube diameter.

SURFACE PREPARATION AND ANALYSIS

We have been working for some time on methods and equipment for preparing and analyzing crystal surfaces. The apparatus employed in most of this work is described in Refs. 4 and 7. We have been using a single crystal nickel specimen, working with the (100) face, and using ion bombardment and electron bombardment for cleaning under ultrahigh vacuum, and photoelectric work function measurements to assess the resulting changes in surface condition. Recently we have added to our program a second approach to surface preparation, namely, continuous deposition of epitaxial films.

Surface Treatment of Crystals

Experiments now in progress should indicate the best methods for surface preparation in our situation, as well as the quality of the surfaces produced. Preliminary work indicates that the purity of the Ar in the bombardment phase of the process and the control of the final low temperature anneal are the most important factors in the cleaning sequence.

The evolution of the apparatus in which these experiments are conducted has taught us several interesting lessons. We have found that the system (mostly glass) works best without traps (both liquid N_2 and zeolite have been discarded) and with only two stages of the oil diffusion pump operating. Mass spectrometer and other types of analysis indicate that the system will not allow significant oil contamination of the specimen for times on the order of 100 hours. The oil used is Convalex 10, which after

aging has proved extremely satisfactory. Another troublesome feature that has now been eliminated was the presence of ceramic feedthroughs in the residual gas analyzer.

A report describing the work in progress will be prepared in early 1968 at the completion of the present series of experiments. At that time we expect to be able to design the needed apparatus for preparing specimens in the molecular beam.

Surface Deposition

We have followed H. Saltsburg's instructions in duplicating his experiments on the deposition of silver (111) surfaces in a molecular beam. We have used his crucible design and have made many silver surfaces on mica substrates. We had some initial difficulties with contamination from volatile materials in the shutter and shields, but these have been eliminated. A few surfaces were verified by X-ray diffraction to be (111). The main problem we faced was shielding the silver system so that it did not excessively contaminate the entire molecular beam apparatus. The technique has been established in a small vacuum setup and is now ready for transfer to the molecular beam apparatus.

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