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INFLUENCE OF THE STATE OF A SURFACE ON THE FORMATION OF A RAREFIED GAS FLOW IN A CHANNEL

O. V. Sazhin and S. F. Borisov

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The results of experimental investigation of free-molecular gas flow in channels with an atomically pure and adsorbed surface are presented. The data obtained made it possible to formulate the basic principles which reflect the character of the effect of the chemical composition of a surface on the gas-dynamic conductivity of the channel. Qualitative interpretation of the obtained experimental results is given within the framework of the existing formalism in the description of the scattering of molecular beams by the surface of a solid body. The diffusion factors ε have been calculated for different surfaces and gases from experimental data. Satisfactory agreement between numerical simulation by the Monte Carlo method and the experimental data is seen.

Under the conditions of superhigh vacuum, conductivity of the elements of technological equipment depends greatly on the character of interaction of gas molecules with the surface of solid bodies. Similarly, heat fluxes are determined by special features of the scattering of gas molecules by a surface. To take into account these phenomena and construct corresponding models that would describe energy and momentum transfer in a gas–solid body system, experimental data are needed. Among other sources of their acquisition are the experiments in which the process of gas flow in channels under high vacuum is studied. The main problem in these experiments is the uncertainty with respect to the chemical composition and structure of the surface.

In the present work, the controllable conditions on the surface are ensured by special preparation of the channel and use of spectroscopic methods of analysis.

Experiment. *Method of investigation.* A method of unsteady flow is implemented in the work. It consists essentially of measuring the time dependence of the pressure p produced at one end of the channel in the volume V_0 in free-molecular gas flow into vacuum (Fig. 1). A capacitance diaphragm micropressure gauge was used to record pressure variation in time [1].

As the characteristic of the outflow process, it is worthwhile to take the conductivity of the channel M, which is a specific flow rate of a gas at a unit pressure difference.

Description of experimental setup. To measure the free-molecular conductivity of the channel, a superhigh vacuum setup was used [2]; it incorporates:

(a) an inflow chamber C_1 (Fig. 1) equipped with a system of purification of the gas studied of active admixtures (nitrogen cryopanel and titanium getter) and a system of automatic recording of pressure (capacitance diaphragm micropressure gauge connected with a computer);

(b) a high-vacuum chamber C_2, evacuated by a helium cryopump, with a built-in mass-spectrometer and an electronic Auger spectrometer;

(c) a channel connecting the two chambers.

Ural State University, Ekaterinburg, Russia; email: oleg.sazhin@usu.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 5, pp. 131–135, September–October, 2001. Original article submitted March 27, 2001.

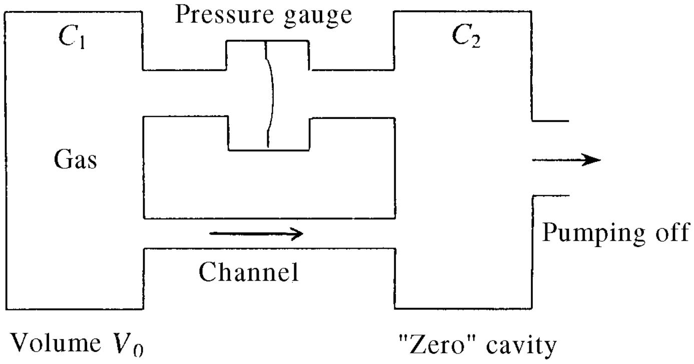


Fig. 1. Schematic of measurements.

The pressure in the chambers was measured by an ionization pressure gauge.

The limiting residual pressure in the high-vacuum chamber C_2 is ~10^{-10} Pa and in the gas inflow chamber C_1 it is 10^{-8} Pa. To obtain a guaranteed composition of the atmosphere, a source of oxygen is also used, which is mounted into the high-vacuum chamber.

During the outflow of gas the pressure in the high-vacuum chamber C_2 did not exceed 0.1% of the pressure at the channel inlet due to the high rate of outgassing by the cryopump (not less than $3 \cdot 10^{-1}$ m^3/sec within the pressure range 10^{-1}–10^{-6} Pa at a maximum He-based admittance of the channel of $8 \cdot 10^{-4}$ m^3/sec).

The use of the capacitance diaphragm micropressure gauge is accounted for by its advantages: indifference to the kind of gas, high sensitivity, high stability of readings, high linearity of the output characteristic, low inertia, and controlled level of sensitivity. The micropressure gauge has the following characteristics:

(a) sensitivity $7.8 \cdot 10^{-6}$ Pa/Hz;

(b) nonlinearity of the output characteristic 10^{-3}%;

(c) instability of readings 0.2 Hz.

The channel is made of thick-walled "pyrex"-type glass and has the form of a cylinder (of radius $r = 7.2 \cdot 10^{-3}$ m and length $l = 1.24 \cdot 10^{-1}$ m). Under the conditions of superhigh vacuum, the inner surface of the channel was coated with metal by vaporizing a thin metal filament stretched along the channel axis. The following metals were used: Ag, Ti, and Mo.

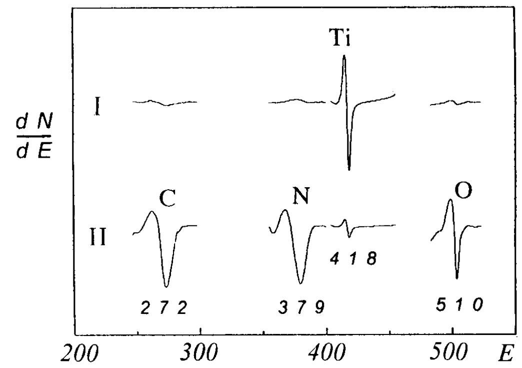
The procedure allowed obtaining an atomically pure surface and keeping the surface clean for the rather long period of time needed for investigation [3].

A number of problems arise in obtaining a thin metallic filament for this technique: if the filament is thick enough, then due to the small specific resistance, say, of pure silver, it is very difficult to heat it to the temperature needed for noticeable evaporation of the metal; at the same time, the reduction of its diameter incurs the possible risk of its breaking because of local superheatings and sagging under gravity upon heating.

In the present work this problem is solved by using as an evaporator a wire consisting of a core and tight winding. Thus, for example, to obtain a thin silver film, the core was a nichrome filament of diameter $3 \cdot 10^{-4}$ m with a 10^{-4}-m-diameter vacuum-annealed silver filament coiled around. The composition of uncontrolled impurities in the winding did not exceed $3 \cdot 10^{-3}$%.

Measurement procedure. Before the measurements were begun, the studied gas was subjected to final purification of active impurities by holding the gas in the volume with nitrogen cryopanel and titanium getter. Mass-spectroscopic analysis showed that the amount of impurities in the gas studied did not exceed 10^{-2}%. Then the gas was supplied through a leak to chamber C_1 until a pressure was reached that provided a free-molecular mode of flow in the channel. At the initial moment of outflow, the pressure of the studied gas was 10^{-1}–10^{-2} Pa.

The subsequent step was the preparation of the channel surface by metal deposition in high vacuum. The parameters of the deposition process were chosen so that the channel surface could be coated by a layer



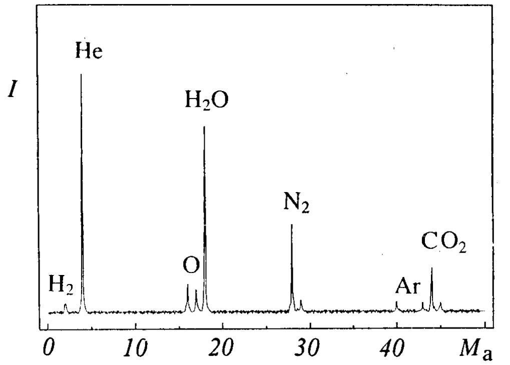


Fig. 2. Derivatives of the Auger spectrum from the surface of the specimen–"witness" recorded immediately after deposition of titanium (I) and after prolonged holding in the atmosphere of residual gases of the vacuum chamber (II).

Fig. 3. Mass spectrum of residual gases in the vacuum chamber.

of the studied metal not thinner than 10^{-8} m. In the process of deposition, the pressure of residual gases did not exceed 10^{-8} Pa. The chemical composition of the surface was controlled by means of an Auger-spectroscopic analysis of a separate specimen, viz., a "witness" located in the high-vacuum chamber C_2. In [2], the data on the chemical composition of a metal surface obtained by deposition in high vacuum are presented; it is shown that under the conditions of this experimental setup the method described can be used for obtaining an atomically pure metal surface and preserving it during the experiment.

Figure 2 shows the derivatives of the Auger spectrum of the surface of the specimen, i.e., the "witness," recorded immediately after titanium deposition and after prolonged holding in the atmosphere of residual gases in the vacuum chamber (several hours). The change in the spectral composition demonstrates the deposition of carbon, nitrogen, and oxygen on the surface of the specimen.

The method of obtaining a surface that could be entirely covered with adsorbed molecules consisted of prolonged holding of the channel with an atomically pure metallic surface in an atmosphere of either oxygen or the residual gases of the vacuum chamber. In the second case, the duration of holding extended to several days. A secondary analysis of possible surface impurities by the chemical composition of residual gases in the high-vacuum chamber was made with the aid of a mass spectrometer. In this case, typical components of the spectrum were H_2, He, H_2O, N_2, Ar, and CO_2. Figure 3 demonstrates a typical mass spectrum of the residual gases in the high-vacuum chamber.

After formation of the surface with the required coating, the free-molecular conductivity of the channel was measured. For this purpose, the valve between the vacuum chambers C_2 and C_1 was opened. The gas flowed through the channel from the inflow chamber C_1 to the high-vacuum chamber C_2, from which it was practically instantly pumped out by the helium cryopump. The data on the experimental dependence of pressure on time were fed into a computer that gave the conductivity of the channel.

Experimental results. In the course of investigations, we obtained data on the effect of the chemical composition of the surface on a free-molecular flow of gases in the cylindrical channel for a number of inert gases: He, Ne, Ar, and Kr. The chemical composition of the channel surface was modified from an atomically pure metallic one to a surface entirely coated with adsorbed molecules.

Table 1 presents the results on the measured reduced free-molecular gas conductivity M^* of the cylindrical channel with an atomically pure metal surface (Ag, Ti) and with a completely adsorbed surface (Me + ads.). The quantity M^* can be presented as follows:

TABLE 1. Reduced Gas Conductivity and Measurement Error $M^* \pm \Delta M^*$ for Different Surfaces and Gases

Surface/Gas	He	Ne	Ar	Kr
Ag	1.62±0.05	1.39±0.03	1.23±0.04	1.15±0.04
Ag + ads.	1.04±0.03	1.03±0.02	1.01±0.02	1.00±0.02
Ti	1.65±0.07	–	1.25±0.04	1.14±0.05
Ti + ads.	1.04±0.02	—	1.02±0.02	1.01±0.02
Mo + ads.	1.03±0.03	1.03±0.02	1.02±0.02	1.00±0.02

$$M^* = \frac{M}{M_{\text{dif}}}, \tag{1}$$

where M_{dif} is the channel conductivity corresponding to fully diffuse scattering of molecules of the specified gas.

The experimental data obtained allow us to formulate the following basic points reflecting the character of the effect of the chemical composition of the surface on the gas-dynamical conductivity of the channel in a free-molecular mode.

1. The gas conductivity of the channel with an atomically pure metal surface substantially exceeds the conductivity of the channel with a surface entirely covered by adsorbate.

2. There is a pronounced dependence of the gas conductivity of the channel with an atomically pure metal surface on the kind of gas.

3. The conductivity of the channel with an atomically pure metal surface seems to be weakly dependent on the kind of metal. Specifically, for the studied Ag and Ti surfaces, the values of gas conductivities coincide within the error of the experiment.

4. The conductivity of the channel entirely covered by adsorbate depends weakly on the nature of the substrate and the kind of gas.

Discussion of experimental results. For comparison and interpretation of the results obtained, we use experimental data on scattering of molecular beams and the formalism, created on the basis of these data, to describe scattering of gas molecules by the surface of a solid body [4].

Following the formalism developed, the scattering of gas by an atomically pure surface of metal can be related to a thermal regime in which thermal vibrations of the surface atoms are a dominating factor determining the character of the interaction. This regime of scattering is characterized by a relatively plane effective surface of interaction. At least, an incident atom "sees" it as such. Here, the interaction in the gas–solid body system occurs at relatively large distances from the surface when a gas atom virtually cannot penetrate into the surface.

The scattering of a gas by a physically adsorbed surface is usually related to a structural regime when the effective surface of interaction is rough and interaction occurs at distances at which gas atoms can penetrate into the surface. As a consequence, this regime of interaction is characterized by the high probability of the gas atoms being captured by the surface and thereafter emitted according to the diffuse law. Under the conditions of this experiment, this fact manifests itself in the gas conductivity of the channel with the adsorbate-coated surface being much lower than the conductivity of the channel with the atomically pure surface of metal.

The effect of the kind of gas on the channel conductivity is attributable to two factors: on the one hand, it is due to the effect exerted on the process of scattering by the mass of a gas atom m_0, which greatly increases from He to Kr and, on the other hand, to the effect of the depth of the potential well D, which also increases noticeably from He to Kr [5]. Thus, within the framework of the present experiment, it was impossible to separate the effect of m_0 from the effect of D, one of the manifestations of which is in a change in the fraction of incident atoms that are captured by the surface and then seem to be emitted according to the diffuse law. It is quite probable that the two effects are not mutually independent. Nevertheless, at present it seems certain that argon, krypton, and xenon are captured by metallic surfaces to a greater extent than helium and neon. Consequently, a larger number of atoms of "light" gases, in comparison with "heavy" ones, is elastically scattered by a surface. This manifests itself in the fact that the gas conductivity of the channel with He and Ne is higher than with Ar and Kr in the thermal regime of scattering.

Interaction in the gas–surface system in a thermal regime occurs at distances at which gas atoms cannot "feel" the properties of the materials from which the surface is made. Therefore, we may assume that distinctive features of scattering in a thermal regime are determined to a greater extent by the characteristics of a crystalline structure than by the chemical nature of the material.

One of the main characteristics of the crystalline structure of a metal is the radius of a surface atom R_s [4]. For example, $R_s = 1.44 \cdot 10^{-8}$ m for Ag, Au, and Ti. Most metals have a nearly coinciding R_s. Thus, one may expect identical scattering of molecules by metallic surfaces, as confirmed by numerous experiments with molecular beams. Thus, for example, in [6], virtually the same scattering indicatrices of Ar atoms on the surface of Ag (111), Pt (111), and W (110) metals were obtained. In the case of our experiment, the fact that the gas conductivity of the channel with an atomically pure surface of Ag and Ti metals does not depend on the kind of metal seems to be attributed to the same character of scattering of inert gases by polycrystalline surfaces of Ag and Ti.

The scattering regime, in which the probability of capture (penetration) is equal to unity, is usually called the regime of adsorption. Obviously, this regime must lack the dependence of scattering parameters on the nature of the surface and kind of gas, since the interaction in the gas–solid body system fully obeys the diffusion law. This dependence still persists in the structural regime, but it is not dominating. As a consequence, the gas conductivity of the channel with an adsorbate-coated surface depends insignificantly on the nature of the surface and kind of gas.

Numerical Simulation. Numerical simulation of gas flow through a cylindrical channel in a free-molecular regime was aimed at obtaining dependences a comparison of which with experiment would make it possible to determine the parameters that characterize the gas–solid body interface. As a model of gas scattering by the surface we used the Maxwell specular-diffuse scheme with the diffusion factor ε being the only free parameter.

As is known, in the case of a long cylindrical channel (i.e., $l >> r$) and of values of ε close to unity, in the regime of a free-molecular flow the diffusion factor ε can be found with the help of the Smoluchowskii formula [7]:

$$M^* = \frac{2 - \varepsilon}{\varepsilon} . \tag{2}$$

The condition imposed on the values of the diffusion factor ε results in the value of M differing slightly from that of M_{dif}.

As the size of the channel is limited ($l/r = 34.4$) and the value of M substantially exceeds that of M_{dif}, the use of the Smoluchowskii formula is incorrect for describing the measurements presented in Table 1. Therefore, the diffusion factor ε was calculated by the Monte Carlo method of direct statistical simulation – a trial particle method (PM) [8].

The gas conductivity of the channel M in a free-molecular regime is determined by the expression

$$M = \frac{1}{4} W S v_{\mathrm{t}} . \tag{3}$$

TABLE 2. Diffusion Factors ε for Different Surfaces and Gases

Surface/Gas	He	Ne	Ar	Kr
Ag	0.71	0.80	0.88	0.92
Ti	0.70	–	0.87	0.92
Me + ads.	0.97	0.97	0.99	1.00

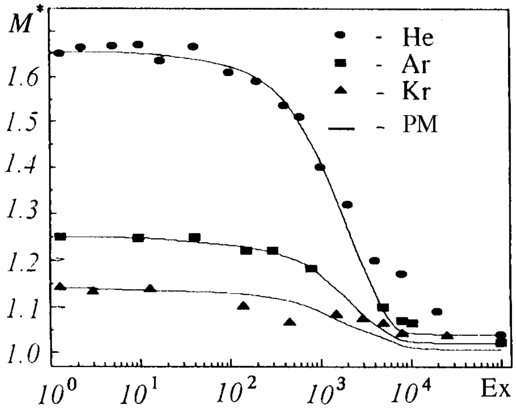


Fig. 4. Comparison of PM calculations with experimental data: reduced gas conductivity M^* of the channel with a titanium surface as a function of surface conditions. Ex, 10^{-4}·Pa·sec.

To calculate the diffusion factor ε for this experimental value of reduced gas conductivity M^* it was necessary to choose a value of ε such that the following relation could be satisfied within the error of calculation:

$$M^* = \frac{W(\varepsilon)}{W(\varepsilon = 1)} . \tag{4}$$

The results of the calculation of the diffusion factors ε for different surfaces and gases are presented in Table 2.

The next step in numerical simulation was the description of the process of change in the gas conductivity M^* in the process of exposure of the channel surface to oxygen. The experimental results obtained earlier [2] formed a basis for comparison.

The numerical simulation was made in two stages. In the first stage, the process of propagation of the oxygen coating of the cylindrical channel surface from the source of oxygen located on one of the channel ends was simulated. In this case, the nonuniform degree of the coating θ of the channel surface with oxygen was determined as a function of the exposure magnitude. In the second stage, the reduced gas conductivity of the channel with the surface coating simulated in the first stage was calculated. It was assumed that at the given point of the channel surface a particle is scattered by the adsorbed surface with the probability equal to the degree of coating θ, and from the atomically pure surface it is reflected with probability $(1 - \theta)$. Reflection from different surfaces was simulated by the Maxwell specular-diffuse model of scattering with the diffusion factors ε presented in Table 2.

As a result of numerical simulation, the dependence of the gas conductivity of the channel on the exposure of the channel surface to oxygen was obtained (Fig. 4). This result is in satisfactory agreement with the experimental data published earlier [2].

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NOTATION

ε, diffusion factor; p, pressure, Pa; E, energy of electrons, eV; V_0, volume, m^3; M, gas conductivity of the channel, m^3/sec; r, radius of the channel, m; l, length of the channel, m; m_0, mass of the gas atom, kg; D, depth of the potential well, J; R_s, radius of the surface atom, m; W, probability of passing through the channel; N, intensity of emission of Auger electrons, rel. units; I, ion current, rel. units; S, area of the input cross section of the channel, m^2; v_t, mean thermal velocity of gas molecules, m/sec^2; θ, degree of coating; Ex, magnitude of exposure, $10^{-4}\cdot$Pa·sec; M_a, atomic units of mass.

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