

Surface Chemical Composition Effect on Internal Gas Flow and Molecular Heat Exchange in a Gas-Solids System

Alexander Ukhov^{*}, Sergey Borisov⁺, and Boris Porodnov^{*}

^{*}Ural Federal University, Ekaterinburg, 620002, Russia

⁺Ural State University, Ekaterinburg, 620083, Russia

Abstract. On the basis of classical knowledge about movement of atoms and lattice theory of F. Goodman and G. Wachman the program modeling helium atom interaction with a three-dimensional crystal tungsten lattice taking into account partial surface covering by chemisorbed oxygen atoms is developed. An efficiency of molecular heat exchange of helium for pure and partially chemisorbed tungsten surface is calculated for different temperatures. Similar model of the surface and procedure of calculations have been applied for description of free-molecular gas flow in long cylindrical channel with clean and fully chemisorbed metal surface. Within the limits of the developed approach the results of calculations for both problems agree well with available experiments with surface contamination control.

Keywords: Gas-surface interaction, accommodation coefficients, free-molecular gas flow, molecular heat exchange.

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INTRODUCTION

The precise experiments show that the surface structure, its physical and chemical heterogeneity, is important to the heat and mass transfer near the surface. Apparently, Knudsen [1] and Clausing [2] were the first who have noticed this effect in their classical experiments and attempted to describe it. The nature, structure and microscopic properties of gas-surface interface primarily start to play an essential role at the rarefied gas conditions when the Knudsen number (Kn) becomes large enough to neglect the contribution of intermolecular collisions in energy and momentum exchange between a gas and a solid body. As it has been shown [3] the efficiency of heat exchange in a nonequilibrium gas-surface system at the free-molecular conditions ($Kn \gg 1$) is completely determined by interface properties. Within the last decades the problem of gas-surface interaction has emerged due to researches' devoted to satellites movement at high altitudes. The use of orbiting mass spectrometers and various gas gauges has allowed establishing the fact that oxygen adsorption on the surface considerably changes a drag coefficient and character of heat exchange of satellites with atmospheric gases [4].

Now the gas-surface interaction problem becomes especially topical in connection with development of a new direction in rarefied gas dynamics – GASMEMS (Gas Flows in Micro Electro Mechanical Systems). As an example one can take Knudsen compressor [5]. The issue is the reduction of device dimensions leads to decrease in value of parameters characterizing regime of gas flow and heat exchange in a gas-surface system. Thus the regime of large Knudsen numbers is reached at rather high gas pressure when adsorption processes play an essential role. Until recently, the quantitative estimation of gas-surface interaction influence on heat and mass transfer represented a considerable problem. In particular, in the reviews containing experimental data related to heat exchange efficiency between rarefied gas and a solid body, one can see an extensive field of non-reproducible results [6]. For example, for approximately the same conditions of molecular heat exchange in *He-W* system, the values of energy accommodation coefficients (EAC) obtained by various authors differ as a factor of 20 (0.02 and 0.4) because of different surface conditions.

More or less reliably reproduced data have been observed only for clean surfaces prepared by the use of special purification procedure in ultrahigh vacuum system [3] or in experiments with molecular beams. An impressive result is presented in paper [7] where tangential momentum accommodation coefficient (TMAC) for *He-Au* system reaches the minimum value ~ 0.1 . Using the molecular beam technique the authors have demonstrated dramatic change in TMAC as a result of surface contamination removal. As for internal gas flow experiments, the value of

TMAC less than ~ 0.9 has been never observed. It is absolutely understandable as all these results were presumably obtained for “dirty” surface.

Thanks to the development of surface diagnostics technique (the electron spectroscopy, scanning probe microscopy) the data acquisition possibilities related to influence of surface structure and its chemical composition on processes of heat and mass transfer have been considerably extended. However experiments with the surface control are still lacking. In Ref. [8] the heat exchange in a gas-metal system has been investigated as a function of surface temperature and its chemical composition using surface control *in situ* with the use of Auger-electron spectroscopy. The experimental concept is based on one of the best realization of this approach that belongs to Thomas [3]. The data on EAC for *He-W* system as a function of surface temperature and surface coverage (surface fraction covered by adsorbed gases) are presented in Fig.1. Energy distribution of Auger-electrons dN/dE as a function of energy E for clean and contaminated surface is shown in Fig.2. The intensity of the peaks corresponds to number of Auger-electrons and therefore to concentration of atoms in a surface layer. It has been shown that the value of EAC at the process of surface contamination removal changes from ~ 0.45 for the surface without special treatment (typical value for “dirty” surfaces) to ~ 0.02 (the result obtained by Thomas [3] for “clean” surface).

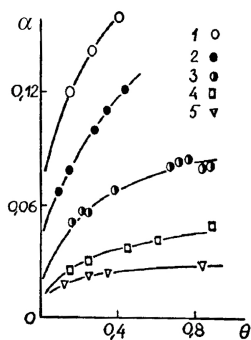


FIGURE 1. Energy accommodation coefficient for *He-W* system as a function of surface coverage and surface temperature T_s : 1 – 298 K; 2 – 446 K; 3 – 968 K; 4 – 1650 K; 5 – 2020 K.

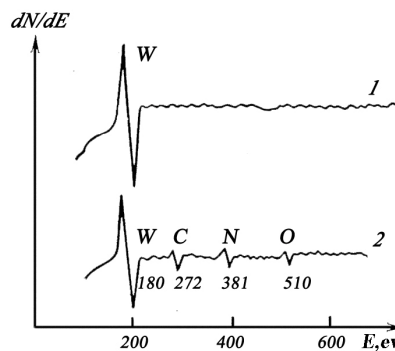


FIGURE 2. Auger spectrum for *W* wire sample at different stages of cleaning: 1 – surface after series of purification cycles; 2 – partially contaminated surface with *C, N, O* atom complexes.

Effect of chemical composition of internal surface of cylindrical channel on free-molecular gas flow has been demonstrated in Ref. [8] as well. In this case, the surface preparation procedure consisted in deposition of titanium film on internal surface of a cylindrical channel. The change in chemical composition of the surface is controlled by Auger-electron spectroscopy using special pilot sample (witness). Mass spectrum data in the vacuum chamber (see Fig. 4) and Auger spectrum of the channel surface (Fig. 5) provide guidance on to the nature of formed adsorbed layer. To provide the guaranteed surface covering, a special oxygen source has been used. The results of gas flow rate measurements as a function of oxygen exposition are presented in Fig. 6.

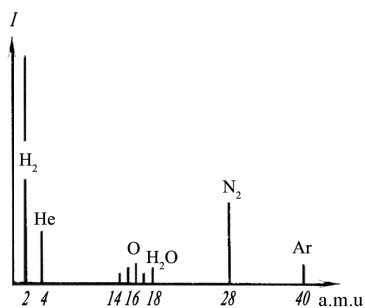


FIGURE 4. Mass-spectrum of residual gases in the vacuum system.

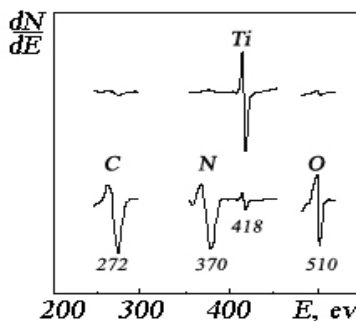


FIGURE 5. Auger-spectrum for “clean” (top) and “dirty” (bottom) surface.

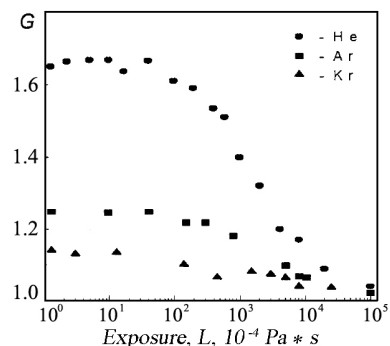


FIGURE 6. Mass flow rate in a cylindrical channel for some noble gases in free molecular regime as a function of oxygen exposure.

The comparison of Auger-spectrum obtained for tungsten wire (Fig. 2) and titanium vacuum deposited surface (Fig. 5) shows that in both cases the surface contamination consists of the same atom complexes. It gives the basis to use the same model of contaminated surface for solving different problems of gas flow and heat exchange with the surface.

Modeling of molecular heat exchange in *He – W* system

On the basis of classical knowledge about movement of atoms and lattice theory of F. Goodman and G. Wachman [9] the program modeling equilibrium and nonequilibrium scattering of helium atoms on a three-dimensional crystal tungsten lattice taking into account partial surface coverage with adsorbed oxygen atoms is developed. The modeling scheme is presented in Fig. 7.

For construction of a detailed picture of gas-surface interaction the physical model of interphase border is considered. The developed approach to the description of this interaction is based on modeling of surface structure of a crystal and interaction potential between gas atom and each surface atom including adsorbed particles. Interaction potentials for *He-W* and *He-O* are taken from [9, 10]. Besides, internal interaction between atoms of a solid body is considered too [11].

The scattering model is constructed on the basis of following assumptions: a) atoms of gas and a solid body represent spheres, their radius and mass correspond to characteristics of real atoms; b) *W* sample is modeled as crystal with *bcc* lattice structure producing thermal vibrations at temperature T_s ; c) forces of interaction between atoms of a crystal are modeled only as ones between the nearest neighbors; d) particles of gas falling on a surface represent the Maxwell's flow at temperature T_g ; e) interaction force between atom *He* and a solid body is calculated taking into account all atoms of a crystal and the atoms adsorbed on it; f) adsorbate is modeled by atoms of oxygen as their primary presence on a surface proves to be true by the data of the electron-spectroscopic analysis (see Fig. 2,4,5); g) the case of thermal scattering of atoms on a crystal surface is considered; h) influence of every possible directions of crystal axes on scattering process is not considered, otherwise, atom of gas interacts with a "flat" surface. Thus, the data obtained as a result of modeling represents integrated behavior of gas – surface system that is realized during all possible processes of scattering.

Modeling of thermal movement of lattice atoms is carried out as follows. At the moment $\tau = 0$ the value of displacement of each atom from equilibrium position is set taking into account corresponding function of distribution at solids temperature T_s . For example, it is known that for tungsten at a room temperature a root-mean-square (rms) displacement of atom from equilibrium position has value $\sigma < 0,1 \text{ \AA}$.

Following to simple physical reasons and assumptions a functional dependence (T_s) describing change in value of rms displacement of lattice atoms as a function of solids temperature is obtained. The character of this function is presented in Fig. 8.

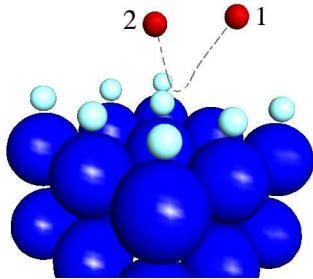


FIGURE 7. Scattering of *He* atom on *W* lattice partially covered by oxygen atoms due to adsorption, $\theta \sim 0.8$: 1, 2 - positions of *He* atom (initial and finite, respectively).

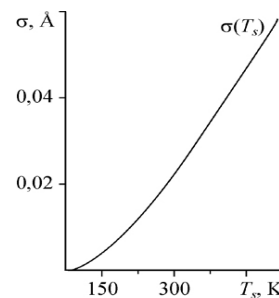


FIGURE 8. Root-mean-square displacement of *W* atom from equilibrium position as a function of solids temperature T_s .

In terms of energy accommodation coefficient an efficiency of molecular heat exchange of helium with clean and partially covered by adsorbed oxygen atoms tungsten surface is calculated for various temperatures. The calculated temperature dependences are compared with the data obtained in experiments with surface diagnostics. Within the limits of the developed approach the results of calculations are in a satisfactory agreement with

experimental data obtained for “equilibrium” and clean surface (Fig. 9) as well as for “nonequilibrium” and a surface partially covered by oxygen atoms (Fig. 10).

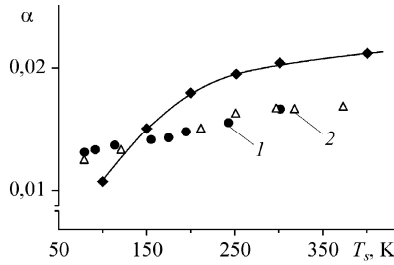


FIGURE 9. “Equilibrium” for clean surface. Simulation (bold line) and experiment: 1 - [3], 2 - [12].

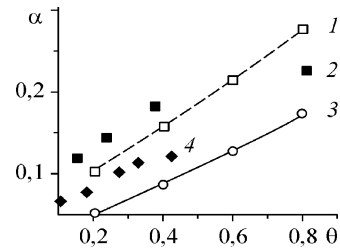


FIGURE 10. “Nonequilibrium” for contaminated surface: 1, 3 – simulation; 2, 4 – experiment [8]. $T_g = 300\text{K}$, $T_s = 298$ (1, 2), $T_s = 446$ (3, 4) K

During debugging of the developed model the value of a bonding force constant k_W that characterizes strength of bond between tungsten atoms is defined. The value of this constant has been obtained as a result of several iterations of repeated modeling the process of *He* scattering on a pure *W* surface. At every step of iteration EAC is calculated according to changing k_W value. The choice of k_W is defined by a principle of the best coincidence received α with experimental data [3, 12]. In the course of modeling of *He* atom scattering on a surface covered by adsorbate to each value of surface temperature a new value of bonding force constant k_{W-Ads} for *W=O* bond is put into conformity. The k_{W-Ads} value similar to k_W is defined by a principle of the best coincidence received α with experimental data. The data on k_{W-Ads} and k_W for different values of surface and gas temperature are presented in Table 1.

Table 1. Bonding force constants values k_W and k_{W-Ads} for *W-W* and *W=O* at different T_s and T_g .

	(1/Å)	T_s (K)	T_g (K)
$k_W, W-W$	500	150–450	150–450
$k_{W-Ads}, W=O$	30	298	300
	280	446	300

Increase of k_{W-Ads} value at rise in surface temperature can be explained on the basis of following reasons. In a real situation with increase T_s the vibration motion of the adsorbed atoms becomes more intensive. Hence, the probability of bond rupture for light atom with other surface atoms and probability of further desorption in the course of such vibrations becomes higher. First of all it concerns hydrogen and other light gases. At further increase of surface temperature one can expect desorption of molecules N_2 , O_2 , H_2O , C_mH_n . The surface reactions with formation of CO , CO_2 , H_2O are also possible. Thus, at rise in surface temperature the number of weakly-joint adsorbed atoms becomes less and it leads to reduction of "sponginess" of the surface structure. In this case helium atoms collide with already more rigid structure *W=O* that starts to collapse at temperature above 2000 K. Hence, the main reason of temperature dependence α for the same surface coating θ consists in change of character of heat exchange between gas molecules and the surface that is caused by change in a structure of adsorbed layer.

Surface chemical composition effects on free molecular gas flow in channel

On the basis of described above formalism of gas-surface interaction by means of computer simulation an attempt to describe influence of chemical composition of internal surface of the cylindrical channel on free-molecular gas flow has been undertaken. Results of calculations have been compared with experimental data on free-molecular gas flow in long cylindrical channel with internal surface covered by silver or adsorbed oxygen and other gases of a vacuum system [13]. Parameters of interaction potential for system “silver – noble gases” have been taken from Ref. [14]. Data on *Ag-Ag* system as well as a function describing root-mean-square thermal displacement of silver atoms from equilibrium position are taken from [15]. Potential parameters for system “noble gases – oxygen” are found in [10].

An example of a gas particle trajectory in the cylindrical channel is shown in Fig. 11. The scheme of *Ar* atom interaction with adsorbate is presented in Fig. 12.

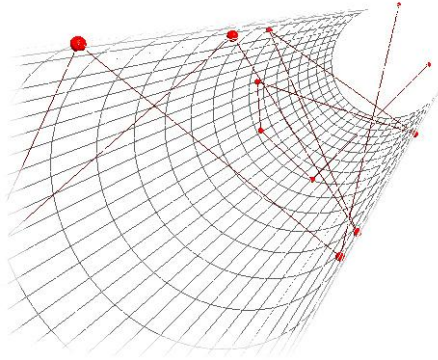


FIGURE 11. Gas molecule trajectory along the cylindrical channel.

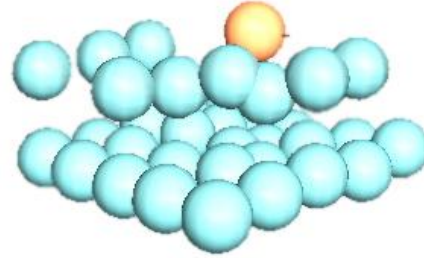


FIGURE 12. The scheme of *Ar* atom interaction with adsorbate.

Results of modeling and experimental data [13] expressed in the form of reduced gas conductivity G of the cylindrical channel in free-molecular regime for different surface conditions and for gases *He*, *Ar*, *Kr* are presented in table 2. The G value is determined as $G = G_{exp} / G_{diff}$, where G_{exp} means experimental gas flow and G_{diff} - calculated gas flow for completely diffuse law of molecule scattering. The type designation “(*Ag*)+*Oxygen*” refers to the metal surface fully covered by adsorbed gases.

Table 2 Reduced gas conductivity of cylindrical channel for some noble gases and different surface composition.

	<i>He</i>		<i>Ar</i>		<i>Kr</i>	
	see [13]		see [13]		see [13]	
<i>Ag</i>	1.62	1.51	1.23	1.285	1.15	1.1
(<i>Ag</i>)+ <i>Oxygen</i>	1.04	2.1	1.01	1.0	1.00	1.0

Modeling process is based on modified Test Particle Monte Carlo method. Gas atoms at the channel entrance have equilibrium Maxwell velocity distribution function at temperature $T_g = T_s = 300$ K. Geometrical parameters of the channel at modeling process corresponded to experimental ones [13], i.e. the relation of length of the channel to its radius was $L/R = 35$. Each act of collision of a particle with an internal channel surface represents scattering of gas atom on three-dimensional crystal silver lattice (fcc) or on a surface completely covered by oxygen atoms. In this case the adsorbate is considered as monolayer of oxygen atoms with bonding force constant k_O that is introduced by analogy with k_W mentioned above. The second physically adsorbed and partially-filled ($\theta = 0.5$) layer represents H_2O , CO , NO etc., i.e. compounds formed by components from spectrum of residual gases of the vacuum chamber (Fig. 4). Atoms of this layer are bonded with the bottom layer of oxygen atoms with bonding force constant k_{O-Ads} by analogy to introduced above constant k_{W-Ads} . The choice of values k_{Ag} , k_O , k_{O-Ads} was defined by a principle of the best coincidence G with experimental data [13]. The obtained by this way values are presented in table 3.

Table 3 The values of bonding force constants k_{Ag} , k_O and k_{O-Ads} for *Ag-Ag*, *O-O* and *O-Ads* systems, respectively.

	(1/Å)	$T_s = T_g$ (K)
$k_{Ag}, Ag-Ag$	285	
$k_O, O-O$	10	300
$k_{O-Ads}, O-Ads$	1	

According to the data presented in table 3 the developed model adequately describes only related gas flows for *Ar* and *Kr* independently on the surface type. As for *He*, calculated gas flow for a case of silver surface quite coincides with experimental data and does not coincide at all when the channel surface is completely covered by adsorbed atoms. Probably, so considerable deviation is caused by quantum-mechanical features of helium atoms interaction with adsorbed layer. Apparently, use of the classical theory in this case not always can yield adequate results.

CONCLUSION

Efficiency of the developed technique for calculation of energy accommodation with consideration of surface chemical composition has been confirmed by experimental results. Observed temperature dependence of energy accommodation at the fixed degree of surface covering by adsorbed atoms can be connected both with change of the degree of non-equilibrium conditions in the system as well as with change of adsorbed layer structure. In particular, with rise in temperature the surface is left by hydrocarbons and there is mainly oxygen.

The developed model of gas molecules interaction with partially contaminated surface can be also effectively used for calculation of gas flow rate in the channels with chemically non-uniform internal surface.

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