Model of Boundary Conditions on Metal Surfaces for Rarefied Gas

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Abstract: Currently, the classical theory discusses issues related to the sliding of liquid and gas along a wall at low external flow velocities. These questions become especially relevant when the surface size is reduced to the nanoscale. The article discusses the formation of sliding conditions and an adsorption layer for an ideal crystalline surface. For gas, the Knudsen layer is proposed to be divided into two parts: an adjacent layer with a thickness of several molecular interaction radii, in which molecules do not collide with each other, and a layer in which the Chapman-Enskog method is defined. The solution for this layer can be found by the small parameter method. For water, there is no Knudsen layer, but adhesion and the formation of a thin stationary layer are possible. Various possible causes of slipping are discussed. The formation of a dislocation from a point defect near the surface, which is a vacancy, is considered. An analysis of the causes of pore clogging during water movement near the surface was carried out. The emphasis is on the change in stress in the metal, taking into account the influence of the moment that occurs when the position of the molecules changes.

Keywords: boundary conditions, kinetic theory, gas-surface interaction, dislocation, vacancies, angular momentum

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1. Introduction

The theory of interaction of a gas with a surface connected with the kinetic theory of gases near surfaces, their interaction with surface molecules and the behavior of near-surface layers of a solid, i.e. it is necessary to solve a conjugate problem. The great practical importance of surface and adsorption processes leads to the need for their detailed study. The equations for macroparameters proposed by the theory are applicable inside the region, but near the boundary, knowledge of the interaction of flow molecules with the surface is necessary. Boundary conditions depend on flow regimes, properties of the surface and medium, and characteristic dimensions of the body. For a rarefied gas with incomplete information about the interaction, usually fictitious boundary conditions (sliding conditions of macroparameters) corresponding to the boundary of the Knudsen layer are specified. The boundary conditions for velocity and temperature (usually at constant density) serve as the boundary conditions for the Navier-Stokes equations. Here the formation of sliding conditions and the adsorption layer is discussed. In layer near the surface formation of a dislocation from a point defect, which is a vacancy is investigated. The emphasis is on the change in stress for the metal, taking into account the influence of the angular momentum that occurs when the position of the molecules changes. Theoretical studies of their interaction of gas with a surface are still in their infancy and in most cases are based on experimental data. Theoretically, specular or diffuse reflection is most often considered [1-6]. Parameter values are expressed through macro parameters. Too many factors influence the interaction of gas with the surface, so the obtained model results are preliminary. For a rarefied gas, at least at low flow rates, we propose to consider a thinner layer equal to several radii of interaction of molecules. The average free path is too long; the interaction of gas molecules with the wall occurs at significantly shorter distances. Gas molecules

inside a thin layer do not collide; collisions occur with surface molecules. The distribution function at the layer boundary is determined by the modified Chapman-Enskog function. According to the classic theory, the density in the system does not change. Therefore, the derivative with respect to time includes derivatives with respect to temperature and velocity, but the number of particles does not change. If we take into account the density derivative [7,8], we obtain the equations S.V. Vallander [9]. The process of interaction of a gas or liquid with a surface is determined by the interaction potentials of the gas flow and molecules of the surface a solid body, as well as the energy of falling particles. In this case, we studied the process of gas adsorption by a surface using the Langmuir method. The potential changes, but for crystalline metals the change in potential during adsorption is considered under the assumption of interaction between molecules of nearest neighbors. Angular momentum is an important component of the power of collective interaction. Basic experimental Gas-surface interaction data refer to monobeam interactions. The velocity distribution qualitatively changes the interaction process and is largely determined by the surface structure. In a liquid near the surface, molecules, such as water, acquire structure due to the interaction of oxygen with molecules of the crystal lattice. Water molecule-dipole. With crystal lattice dipole-dipole interaction occurs. The position of oxygen, due to the structural features of the water molecule, determines the next adsorption layer, and several layers are required to restore the nature of the distribution of water in the volume. Consequently, a process of relaxation of the "position" of the molecule near the surface must occur. It takes time. When water flows around nanostructures, sliding is observed in experiments. Experimental studies show that when flowing around hydrophilic surfaces, the sliding length is several nanometers, and over hydrophobic surfaces - tens of nanometers. The Navier-Stokes approximation may not work at small scales, especially near solid-liquid boundaries. Adhesion conditions may not be correct. The

surface to volume ratio can be high. Various transition regimes may exist near the surface. The role of surface effects is important [10,11]. For liquids near a smooth surface, a model with a thin layer of stationary liquid can be proposed. The width of the layer is determined by the magnitude of dynamic friction (an analogue of turbulent flow). Mathematically, for a normal turbulent layer and taking into account the contribution of the angular momentum, a logarithmic function is obtained. A singularity appears on the surface. You can remove it using the suggested supposition. An important factor is information about the increase in sliding length with a decrease in the interaction potential of molecules. The sliding mechanism has not yet been determined. The main thing is that sliding occurs at the molecular level. The Maxwell distribution does not depend on the interaction between particles and is valid not only for gases, but also for liquids. In the proposed model, an important role is assigned to two factors: the distribution of molecules by speed, the change in potential under the influence of torque, and the more rarefied distribution of water molecules compared to molecules of a solid body. Phonons and the influence of electrons are not taken into account. The study is limited to mechanical influences. The distribution of speed and torque provides surface roughness, while simultaneously leading to a smoothing of the action of potentials between water molecules and molecules of a crystalline solid. The Lennard-Jones interaction potential between water and metal, the potential between solid molecules is the Morse potential. More complex potentials are also used, but the ones shown are more often used. The existence of the sliding effect is most often explained by the assumption of the presence of air near the surface and on the walls of the capillaries. Estimates show that the presence of air can influence the occurrence of the transient process. With a stable flow, even with a specially structured surface, air retention in the recesses is doubtful. A feature of water in a calm state is the formation of accumulations (dimers, trimers, etc.). There is no answer to the question of maintaining agglomeration during

fluid movement. Size ratio is also an important factor. Internuclear O–H distances are close to 0.1 nm, the distance between the nuclei of hydrogen atoms is 0.15 nm, and the angle between H–O–H bonds is 104.5°. Minimum distance between aluminum molecules L = 3.1038 A., water molecule size $r_{(0)}$ = 31.8 A., mean free path γ = 21.6÷36.6, cluster size 9.06÷1.22 nm. [12]. Some molecules are in a free state. It is these molecules that carry out transport processes in liquids. The size ratio indicates the possible overlap of the gaps between surface molecules by a water molecule. For capillaries with a radius on the order of the cluster radius, sliding is possible due to contact with the wall of a small part of the cluster. If long-range forces are not enough to destroy the accumulation, then sliding can be caused by the same reasons. The speed of falling onto the cluster wall is less than the speed of falling of a free molecule, so the cluster must stick to the surface. To illustrate the effect of torque on small scales, we consider the problem of the effect of torque on the top of a surface molecule if the surface is stepped (close interaction approximation). The surface structure may change during operation. The most important role in changing the surface structure and the formation of cracks is played by defects in the surface and adjacent metal layers associated with the interaction of dislocations. This work examines the initial stage of dislocation formation near a point defect (vacancy). It is generally accepted that the formation of a vacancy is accompanied by relaxation of nearby atoms. Thus, solving the problem of interaction of gas and liquid with a metal surface requires an understanding of the molecular structure of both the medium and the surface, as well as knowledge of the structural features of the surface layers of the metal; therefore, it is necessary to solve the problem of superposition.

2. Kinetic of sliding conditions and adsorption layer.

The process of interaction between gas and liquid is greatly influenced by the state of the surface and the presence of adsorbed molecules. In addition, the presence of an adsorbate affects the arrangement of atoms in subsequent layers. If the distribution function of falling monatomic molecules is known, then the interaction of the gas with the surface is determined by the transformation function - the probability density of the reflection of an atom with a given speed of incidence at a defined speed of reflection. In macro-description, experimentally determined accommodation coefficients are used [1-3]. In theoretical studies of the flow of rarefied gas around bodies, the conditions of specular or diffuse reflection, determined experimentally, are taken into account. At high adsorbate concentrations, along with a shift along the normal to the surface, a shift in the lateral direction also occurs. The result is a change in the interaction potential of metal atoms with gas and liquid. It is not possible to fully consider the processes of interaction. Therefore, only some of the possible effects are investigated here. It is known (Wentzel model) that wettability affects the sliding process. Molecular dynamics modeling shows an increase in slip with a decrease in the interaction potential of molecules. "Apparently, the thinnest layer of liquid molecules adheres tightly to the solid, but the velocity gradient is so large that the molecules move over this layer". [11, 12].

Consider the classical Knudsen layer. Approximately 38 percent of the molecules contained at the outer boundary will reach the surface. It is this value that we will consider at the boundary of our layer. Only a small part with low energy can be adsorbed on the surface. The amount depends only on the temperature. Most of the molecules will be reflected, approaching at a distance equal to the radius of interaction of the gas molecule and the surface. The distance depends on the interaction potential of the molecules. These molecules will return to the outer boundary. The adsorption time of the main air components having a heat of adsorption of 20 MJ/kmol is 10^{-10}s at room temperature and $1s$ at liquid nitrogen temperature. The equations for macroparameters obtained in the kinetic theory are applicable inside the region, but near the

boundary it is necessary to know the interaction of the flow molecules with the surface. In the case of incomplete information about the interaction, fictitious boundary conditions (slip conditions) are specified corresponding to the boundary of the Knudsen layer. The boundary conditions for velocity and temperature (at constant density) serve as the boundary conditions for the Navier-Stokes equations. Here it is proposed to split the task into two. For a rarefied gas, at least at low flow rates, it is proposed to consider a thinner layer equal to several molecular interaction radii. The mean free path is too long, interactions of gas molecules with the wall occur at much shorter distances. The gas molecules inside the thin layer do not collide; collisions take place with surface molecules. The distribution function at the layer boundary is determined by the modified Chapman-Enskog function, which takes into account the change in the number of particles. The interaction process is determined by the interaction potentials of the flowing gas and solid surface molecules, and the action of the angular momentum on the structured surfaces is taken into account.

Molecules moving towards the wall must be divided into three groups: molecules with low speed, which subsequently stick to the wall, molecules with medium speed, which are reflected from the wall, and molecules with high speed, which penetrate the wall. The boundaries of the ranges are determined by the energy of accommodation for a specific gas and surface material and by the speed of the incident molecule. When solving the problem, it must be remembered that the interaction potential depends on the interplanar distance between the surface layer and the previous one, which depends on the orientation of the crystallographic surface. In many cases, the distance increases, which entails a change in the interaction potential. In this case, the role of collective effects is reduced. Having obtained the distribution function at the layer boundary it is necessary to solve the Boltzmann equation in the layer from this boundary to the Knudsen layer boundary by the small parameter method using the Chapman-Enskog function. This can be done by a small change in the distribution

function over the mean free path. Accounting for collective interactions was first performed by Langmuir. For crystalline metals, the change in the potential during adsorption was considered under the assumption that the molecules of the nearest neighbors interact. In this work, the same assumption is used, taking into account the angular momentum. The purpose of the analysis is a theoretical study of the process of gas adsorption by the surface. Usually, when determining the slip length, it is considered that the distribution function on the surface has the form

$$f_r = f_r \left(0, \xi_x, \xi_y > 0, \xi_z\right)$$
$$= n_r \; (\frac{h_r}{\pi})^{\frac{3}{2}} \; e^{-h_r \; \xi^2}.$$

The formula is written on the assumption that the vertical and horizontal velocities are zero. Here r is for reflected molecules,

$$h^{\pm} = \frac{m}{2kT^{\pm}} \; .$$

When calculating macro parameters on the surface, for example, the number of particles

$$n(0) = \int_{\xi_y > 0} f_i d\xi + \int_{\xi_y < 0} f_r \; d\xi$$
$$= \frac{n(0)}{2} + \frac{n_r}{2} + O\left(\in \frac{df_0}{dy}\right).$$

The difference in the distribution function seems to be significant, since for the reflected particles the vertical component of the velocity is equal to zero under the condition of impermeability, for the incident particles the full velocity is taken. Similarly for other macro parameters. Boundary condition for the internal case

$$n(0) = \int_{\xi_y > 0} \xi_y \; f_i d\xi + \int_{\xi_y < 0} \xi_y f_r \; d\xi = 0.$$

Under the assumption of the absence of adsorption and the equality of the macrovelocity on the surface to zero, due to the difference in velocities, a paradox arises, which can be resolved only on the assumption that the gas is immobile near the surface. The probabilities of the equilibrium distribution function on the surface on the right and on the left differ in magnitude. As a result, the number of falling particles and the probabilities of moving to the right and to the left differ. The number of incident particles is determined by the values [23]

$$\nu_\text{п} = \frac{n v_S}{2\sqrt{\pi}} \{ e^{(\frac{U_x}{v_S})^2}$$
$$+ \sqrt{\pi}\frac{U_x}{v_S}\left[1 + \Phi\left(\frac{U_x}{v_S}\right)\right]\}$$

$$\nu_\text{п} = \frac{n v_S}{2\sqrt{\pi}} \{ e^{(\frac{U_x}{v_S})^2}$$
$$+ \sqrt{\pi}\frac{U_x}{v_S}\left[1 - \Phi\left(\frac{U_x}{v_S}\right)\right]\}$$

The following designations are adopted here: $\nu_\text{п}$ is the number of falling gas molecules, v_S is the most probable velocity of gas molecules. The difference in probabilities leads to the probability of directed movement along the inner boundary. In addition, two different forces arise during the interaction: one along the surface, the second vertically to the surface. The lattice parameters of aluminum are 4.050 Å. Under normal conditions, interacting with atmospheric oxygen, aluminum is covered with a thin ($2\text{-}10^{-5}$ см)) film. Oscillating changes in the interplanar spacing near the surface are on the order of 10% or less (depending on the temperature and face: loose or close-packed). For example, it is known that for tungsten at room temperature, the root-mean-square displacement of an atom rom the equilibrium position is < 0.1 Å . The motion of phonons should not affect the adsorption processes, except for the case of long-wavelength phonons, since the shift of surface atoms is $0.1 \div 0.5$ Å. In the inelastic interaction of gas and phonons, part of the energy of the gas is spent on the excitation of phonons along the direction perpendicular to the surface, which corresponds to the flow dissipation process. The creation of the forest prevents gas and phonons from interacting. In addition, contact with a solid body is reduced. However, the processes of scattering of atoms and molecules proceed differently for small and large irregularities and depend on the height of the roughness, since the contribution of the moment changes. The amplification of the action of the sliding moment occurs as the result of the difference between the vertical and horizontal forces. Moment creates a force acting up or down. The angular momenum is involved in the growth of the forest. Forest growth, as follows from the next point, is

associated with the emergence of dislocations to the surface. For example consider the step [10].
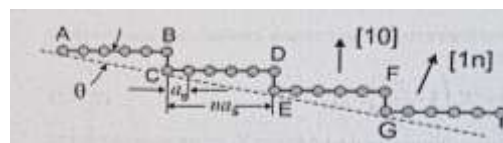

Fig. 1. Model of a surface with a terrace

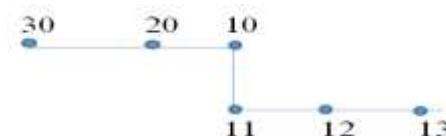Let us schematically depict one stage

*Fig.*2. One step diagram...

Let us denote the distance between molecules as unity. Then we get that the force between molecules (10.12) is equal to $F_{ix}(\sqrt{2})$, (10,13) $= F_{ix}(\sqrt{5})$; between molecules (20,10) $= F_{ix}(1)$, $F_{ix}(2), \dots$. The total forces on the right and left will be different, a moment will arise - the corresponding force that will pull up if the step goes down. For a step up, the force will pull down. The temperature dependence is step goes down. For a step up, the force will pull down. The temperature dependence is responsible for the distance that a molecule approaches the surface. Thus, when studying surface effects, an important role should be assigned to the impulse and collective effects from the influence of torque. In quantum theory, particles are also treated as points. In the study are restricted to closed systems. Mainly considered pairwise interactions or system of noninteracting particles. When considering several particles simultaneously limited by additivity of extensive quantities if no charged particles. In fact, each particle is far enough away from each other. In the analysis of the interaction of charged particles the presence of all the particles is taken into account the potential to include the interaction of electrons and ions or by hypothetical distribution function or solution of the Poisson equation with the charge distribution around the core particles (computational methods particle-

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particle, particle mesh) [5]. These methods are used to calculate the potentials of metals and equilibrium conditions when considering the interaction of metal atoms with gas, corresponding to the operator angular momentum $\xi_i \cdot \frac{\partial}{\partial x_i}\left(x_j \frac{\partial \rho}{\partial x_j}\right)$. Consequently, for the wave function $\xi_i \cdot \frac{\partial}{\partial x_i}\left(x_j \frac{\partial^2 \psi}{\partial x^2}\right)$ and consider instead the function $F(x, y, z, p_x, p_y, p_z)$ the function $F(x, y, z, p_x, p_y, p_z, yp_z - zp_y, xp_z - zp_x, xp_y - yp_x)$ in this.

The bond between the oxygen atom and the hydrogen atoms is polar, because oxygen attracts electrons more strongly than hydrogen The internuclear $O - H$ distances are close to 0.1 nm, the distance between the nuclei of hydrogen atoms is 0.15 nm, and the angle between the $H - O - H$ bonds is 104.5 dimension case, the effect of these variables willt be traced. Using the classical variant leads to a linear dependence of the moments that can be realized only under additional conditions. Interaction with water is determined by the structure of the molecule and the change in the surface potential (loosening). The H_2O molecule has an angular structure and has a dipole moment. From the point of view of the theory of valence bonds, the bonding in the H_2O molecule is determined by the interaction of the valence 2s and 2p electrons of the O atom with the 1s electrons of the H atoms. Four of the six valence electrons of the O atom that do not participate in the formation of OH bonds form two couples). These allow the oxygen atom of the H_2O molecule to bind to other molecules. In this case, the water molecule exhibits the properties of an electron donor. In the case of adsorption, unshared electron pairs of molecules are able to form bonds both with surface atoms and with other molecules adsorbed on the surface. There is no Knudsen layer. The water molecule has two positive and two negative poles and, therefore, in most cases behaves like a dipole (i.e., on the one hand, a positive charge, on the other, a negative charge [sediment]. The cluster nature of water in the case of dipole interaction at low speeds does not allows water to penetrate in the surface.

3. Formation of a dislocation from a point defect.

In the mathematical theory of plasticity, hardening and fracture, experimental data are taken as initial data. The theory of elasticity is more developed, but even in the region of low stresses it is not possible to explain some effects. The physical mechanism is not studied in such theories.

During plastic deformation, anisotropy occurs, that is, the acquisition of different mechanical properties in different directions [12-20]. There are no ideal crystal lattices. The formation of dislocations near the surface and deep in the material occurs in different ways. Apparently, forces act near the surface, ensuring that, under the influence of loads, the defect reaches the surface and the formation of short dislocations. The role of angular momentum is significant in all cases. Experimentally determined critical shear stresses for pure metals are several orders of magnitude lower than theoretically determined ones. Taking into account structural defects leads to closer theoretical results. Let us consider the initial stage of dislocation formation. Let there be a vacancy inside the material. In equilibrium, the forces arising from lattice distortion are not sufficient to move molecules. Let there be free space near the border. For the Lennard-Jones potential

$$F(a) = -4\varepsilon\left[-12\frac{\sigma^{12}}{(a)^{13}} + 6\frac{\sigma^6}{(a)^7}\right],$$
$$F(2a) = F(2a) + 4\,F(a\sqrt{2}) + 4 \cdot F(2a\sqrt{2}),$$
$$F = 0 = F(2a) + 12F(a\sqrt{2}) =$$
$$= -4\varepsilon\left[-12\frac{\sigma^{12}}{(2a)^{13}} + 6\frac{\sigma^6}{(2a)^7}\right] - 12\{$$
$$-4\varepsilon\left[-12\frac{\sigma^{12}}{(a\sqrt{2})^{13}} + 6\frac{\sigma^6}{(a\sqrt{2})^7}\right],$$
$$F(r + \Delta r) = -4\varepsilon\left[-12\frac{\sigma^{12}}{(r+\Delta r)^{13}} + 6\frac{\sigma^6}{(r+\Delta r)^7}\right].$$

From the equation you can determine the equilibrium point r_0. Full force
$$F_c = F + \gamma, \quad \gamma\text{- stresses acting on one}$$
molecule.

Let us consider the relationship between the forces of the "correct" and distorted lattices.

$$\varphi = \frac{-4\varepsilon[-12\frac{\sigma^{12}}{(2a)^{13}} + 6\frac{\sigma^6}{(2a)^7}}{-4\varepsilon[-12\frac{\sigma^{12}}{(a)^{13}} + 6\frac{\sigma^6}{(a)^7}} \approx 0.008.$$

The usual experimental value is ≈0.1. The equilibrium position is unstable. Any small disturbance, such as phonons, or an increase in load can lead to reverse motion due to repulsive forces. Under load, due to changes in the position of the molecules, the center of inertia shifts, shifting during tension in the direction of the creating stress, which creates a moment. The angular momentum creates an additional force directed perpendicular to the stretch. The values of this force are of the order of $\sigma\_m= \Delta\_1/2a \ F(2a)$. Consequently, there will be a stop at the equilibrium point. If the loads remain the same, an oscillatory mode will occur. Further propagation requires a significant increase in voltage. This process probably requires a relaxation process. The calculations is performed for all surrounding points. Due to symmetry, the number of points are reduced. As the load increases, the calculations are repeated. The length of the dislocation is determined by the applied energy. Criteria for the energy state of the energy balance can be found in [11,12]. In the presence of energy, the dislocation pushes the atom to the surface. Having no resistance, the main molecule will rise, the neighboring ones will be pulled up and a "whisker" will be formed. Mechanical research methods will not give results, since the application of a load changes the surface.

4. Conclusion

The great practical importance of surface and adsorption processes leads to the need for their detailed study. The equations for macroparameters proposed by the theory are applicable inside the region, but near the boundary, knowledge of the interaction of flow molecules with the surface is necessary. Boundary conditions depend on flow regimes, properties of the surface and medium, and characteristic dimensions of the body. In the article the formation of sliding conditions and the adsorption layer is discussed. The Knudsen layer is proposed to be divided into two parts: a nearby layer with a thickness of several molecular interaction radii, in which molecules do not collide with each other, and the another of the layer; where the Chapman-Enskog solution can exist, considered by the small parameter method. The formation of a dislocation from a point defect, which is a vacancy, has been studied. The emphasis is on the change in stress in the metal, taking into account the influence of the angular momentum that occurs when the position of the molecules changes. It has been shown that the change in the interaction potential of molecules near a vacancy by two orders of magnitude and the action of the angular momentum creates the conditions for the formation of a crack.

To confirm the conclusions obtained, additional calculations by the molecular dynamics method and corresponding experiments on the effect of directional velocity on adsorption processes are necessary, since the distribution functions are different. A similar study of the influence of impurity molecules is also necessary.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

The authors equally contributed in the present research, at all stages from the formulation of the problem to the final findings and solution.

Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.