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Abstract

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KINETIC EQUATION OF AN ADSORPTION MONOLAYER

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At atmospheric density and low temperatures, an adsorption layer forms on the surface of a body in a flow; this layer may be so substantial that it completely determines the character of the interaction of the gas flow with the surface. As the density decreases and at high velocities of motion, the number of adsorbed particles decreases both because of spontaneous (thermal) desorption and because of "knock-out" by particles of the flow. Therefore the individual properties of the surface begin to influence the character of reflection of gas particles, which entails a change in the flow and in the aerodynamic characteristics.

In the present note a kinetic equation of an adsorption monolayer is obtained, which must be coupled to the equation for the distribution function describing the external flow when solving boundary-value problems of the flow of a rarefied gas past bodies. This is done with the aid of the idea of a statistical ensemble of particles in the space of states and time—an idea that was used in the space of states in work (^{1}).

Let the surface be controllable with respect to orientation and physicochemical properties; let the external flow consist of structureless particles and be described by a function $f(\mathbf{r}, \mathbf{u}, t)$, having the meaning of the density of the mathematical expectation of the number of particles in an element of phase volume; let ds be an elementary surface area adjacent to the radius vector $\mathbf{r}_s$; let $\vartheta(\mathbf{r}_s, t)\, ds$ be the number of particles adsorbed on ds at the instant t; let $T_w(\mathbf{r}_s, t)$ be the surface temperature; and let $Q_\lambda(\mathbf{r}_s, \vartheta)$ be the binding energy of an adsorbed particle with the surface, where the index λ characterizes the type of bond.

Probability of energy exchange. Let $\widetilde{T}_1(\mathbf{u}, \mathbf{r}_s, T_w, \varepsilon)\, d\varepsilon$ be the probability that, in a collision of a particle with a clean portion of the surface, an energy from the interval $[\varepsilon, \varepsilon + d\varepsilon]$ will be transferred to the latter, provided that before the collision the particle had velocity $\mathbf{u}$; $\widetilde{T}_2(\mathbf{u}, \mathbf{r}_s, T_w, \varepsilon)$ has the same meaning as $\widetilde{T}_1$, but for a portion of the surface occupied by adsorbed particles. Then the probability density for energy exchange in a collision with an arbitrary portion of the surface has the form

$$\widetilde{T}(\mathbf{u}, \mathbf{r}_s, T_w, \vartheta, \varepsilon) = \vartheta(\mathbf{r}_s, t)\sigma \widetilde{T}_2 + (1 - \vartheta(\mathbf{r}_s, t)\sigma)\, \widetilde{T}_1,$$

where $\sigma = 1/N$; N is the maximum possible number of adsorbed particles in the layer under consideration per unit area.

Finding the functions $\widetilde{T}_1$ and $\widetilde{T}_2$ is a major independent problem.

Probability of desorption. $\Psi(\mathbf{r}_s, \vartheta, t)\,dt$ is the probability of desorption of a particle during the time dt. Desorption may occur spontaneously, owing to energy fluctuations, and owing to knock-out by particles of the flow, i.e., one may write

$$\Psi = \sum_{\lambda} \Phi_\lambda \psi_{1\lambda} + \sum_{\lambda} \Phi_\lambda \psi_{2\lambda},$$

where Φ_λ characterizes the occurrence frequency of different bonds, $\psi_{1\lambda}\,dt$ is the probability of spontaneous desorption for a given type of bond during the time dt, and $\psi_{2\lambda}\,dt$ is the probability of desorption due to knock-out for a given type of bond

over dt. $\{\Phi_\lambda\}$ can be found by methods of statistical physics, $\psi_{1\lambda} = 1/\tau_\lambda$, where τ_λ is the mean residence time of an adsorbed particle on the surface for a given type of bond and temperature.

For model calculations one may use the known Frenkel expression $\tau_\lambda = \tau_0 \exp(Q_\lambda / kT_w)$, where $\tau_0 \sim 10^{-13}$ sec.

For the calculation of $\psi_{2\lambda}$ one may use the scheme of local heating proposed by P. L. Kapitsa (^{2}) to explain electron ejection, but which has found successful application to cathode sputtering.

Successive application of the scheme leads to the expression

$$\psi_{2\lambda} = \iiint_{(u_n<0)} \int_0^\infty \Big\{ |u_n| f(\mathbf{r}_s, \mathbf{u}, t)\, \widetilde{T}(\mathbf{u}, \mathbf{r}_s, T_w, \theta, \varepsilon) \times$$

$$\times \iint_{(s')} \left[1 - \exp\left(\int_0^\infty \sum_{\lambda} \Phi_\lambda \psi_{1\lambda}(\mathbf{r}'_s, T, \tau)\, d\tau \right) \right] ds' \Big\}\, d\varepsilon\, d\mathbf{u},$$

where (s') denotes the plane whose normal coincides with the normal to the surface at the point under consideration,

$$T = -\frac{\varepsilon}{\rho c (2b\sqrt{\pi t})^3} \exp\left[-\frac{(x_s - x'_s)^2 + (y_s - y'_s)^2 + z_s^2}{4b^2 t} \right].$$

The probability of not being desorbed during a finite time interval can be represented through Ψ in the form

$$R(\mathbf{r}_s, \theta, t_0, t) = \exp\left[-\int_{t_0}^{t} \Psi\, dt\right].$$

Probability of adsorption. The probability of adsorption K in the general case is determined through the function $\widetilde{T}$

$$K(\mathbf{u}, \mathbf{r}_s, T_w, \theta) = 1 - \int_{-\infty}^{mu^2/2} \widetilde{T}(\mathbf{u}, \mathbf{r}_s, T_w, \theta, \varepsilon)\, d\varepsilon,$$

where m is the mass of the incident particle, and $\mathbf{u}$ is its velocity before collision.

According to the Langmuir scheme (^{3}), adsorption occurs only upon collision with a clean portion of the surface. In this case

$$K = (1 - \theta\sigma)\left(1 - \int_{-\infty}^{mu^2/2} \widetilde{T}_1\, d\varepsilon\right).$$

Equation of the adsorption layer. Using the introduced functions R and K and carrying out a statistical count of particles in time on a surface element ds, we obtain the desired equation

$$\theta(\mathbf{r}_s, t) = \theta(\mathbf{r}_s, t_0) R(\mathbf{r}_s, \theta, t_0, t) +$$

$$+ \int_{t_0}^{t} R(\mathbf{r}_s, \theta, \tau, t) \iiint_{(u_n<0)} |u_n| f(\mathbf{r}_s, \mathbf{u}, \tau) K(\mathbf{u}, \mathbf{r}_s, T_w, \theta, \tau)\, d\mathbf{u}\, d\tau. \qquad (1)$$

In the stationary case the equation has the form

$$\theta(\mathbf{r}_s) = \theta(\mathbf{r}_s) R(\mathbf{r}_s, \theta, 0, a) +$$

$$+ \int_{0}^{a} R(\mathbf{r}_s, \theta, \tau, a)\, d\tau \iiint_{(u_n<0)} |u_n| f(\mathbf{r}_s, \mathbf{u}) K(\mathbf{u}, \mathbf{r}_s, T_w, \theta)\, d\mathbf{u}, \qquad (2)$$

where a is an arbitrary constant having the dimension of time and not equal to zero.

Equation (1) or (2), together with the kinetic equation for the function f describing the incident flux, constitutes a closed system of equations. The dynamical acts of interaction are described by functions which, within the assumptions made, can be found with arbitrary accuracy by means of the methods of theoretical and experimental physics. The scheme for deriving equation (1) can be extended to the case of a gas with internal degrees of freedom.

Some solutions of equation (2). In the stationary case, if adsorption is considered according to the Langmuir scheme, "knockout" according to the thermal scheme, and the functions K, Φ_λ, $\psi_{1\lambda}$, $\widetilde{T}_1$, $\widetilde{T}_2$ do not depend on θ, then equation (2) is transformed into a quadratic algebraic equation, whose solution has the form

$$\theta = \frac{-(A+\sigma F) + \sqrt{(A+\sigma F)^2 + 4BF}}{2B}, \tag{3}$$

where

$$A = \sum_\lambda \Phi_\lambda \psi_{1\lambda} + \iiint_{(u_n<0)} \int_0^\infty |u_n| f(\mathbf{r}_s, \mathbf{u}) \widetilde{T}_1 \times \left\{ \iint_{(s')} \left[1 - \exp\left(\int_0^\infty \sum_\lambda \Phi_\lambda \psi_{1\lambda}\, d\tau \right) \right] ds \right\} d\varepsilon\, du,$$

$$B = \sigma \iiint_{(u_n<0)} |u_n| f(\mathbf{r}_s, \mathbf{u})\, [\widetilde{T}_2 - \widetilde{T}_1] \times \left\{ \iint_{(s')} \left[1 - \exp\left(\int_0^\infty \sum_\lambda \Phi_\lambda \psi_{1\lambda}\, d\tau \right) \right] ds \right\} d\varepsilon\, du,$$

$$F = \iiint_{(u_n<0)} |u_n| f(\mathbf{r}_s, \mathbf{u})\, K\, du.$$

If the flux is free-molecular and the surface is homogeneous in its physicochemical properties, then A and B can, with great accuracy, be represented in the form

$$A = \psi + \frac{\Gamma(4/3)\, k^{4/3} \rho}{8\pi m \tau_0 \chi (\rho_1 c)^{1/3} Q^{4/3}}\, |u_{0n}(\mathbf{r}_s)| \int_0^\infty \varepsilon^{4/3} \widetilde{T}_1\, d\varepsilon,$$

$$B = \sigma |u_{0n}(\mathbf{r}_s)| \frac{\Gamma(4/3)\, k^{4/3} \rho}{8\pi m \tau_0 \chi (\rho_1 c)^{1/3} Q^{4/3}} \int_0^\infty \varepsilon^{4/3} (\widetilde{T}_2 - \widetilde{T}_1)\, d\varepsilon,$$

where Γ is the gamma function, k is Boltzmann’ s constant, ρ is the particle density in the incident flux, m is the mass of the gas particles, ρ_1 is the density of the surface material, χ, c are respectively the thermal conductivity and heat capacity of the surface, and u_0 is the velocity of the incident flux.

If the external conditions are equilibrium ones, the surface is homogeneous, "knockout" practically does not occur, and the adsorption probability K is constant, then formula (3) becomes the well-known Langmuir isotherm.

Some solutions of equation (1). In the case of free-molecular flow or weak dependence of the incident flux on θ, it is reasonable to consider nonstationary adsorption under stationary external conditions. Then, if adsorption proceeds according to the Langmuir scheme and "knockout" in accordance with the thermal scheme, the solution of the nonlinear integral equation (1) has the form

$$\theta(\mathbf{r}_s, t) = \frac{A_1 + A_2 c \exp\left(-\frac{A_1+A_2}{2}\, t\right)}{2B\left[1 - c\exp\left(-\frac{A_1+A_2}{2}\, t\right)\right]}, \tag{4}$$

where

$$C = \frac{2B\theta(\mathbf{r}_s, 0) - A_1}{2B\theta(\mathbf{r}_s, 0) + A_2},$$

$$A_1 = -(A + \sigma F) + \sqrt{(A+\sigma F)^2 + 4BF},$$

$$A_2 = (A + \sigma F) + \sqrt{(A+\sigma F)^2 + 4BF}.$$

As $t \to \infty$, (4) passes into (3).

If the "knock-out" has practically no effect $\left(A \to \sum_\lambda \Phi_\lambda \psi_{1\lambda},\ B \to 0\right)$, the external conditions are equilibrium ones, the surface is homogeneous, and the probability of adsorption is constant, then formula (4) becomes the following:

$$\theta = \frac{\sigma^{-1}\gamma(T)p}{1+\gamma(T)p} + \left[\theta(\mathbf{r}_s, 0) - \frac{\gamma(T)\sigma^{-1}p}{1+\gamma(T)p}\right] \exp\left[-(\alpha(T)\sigma p + \psi_1)t\right], \tag{5}$$

where α and γ are certain computable functions of temperature, and p is the gas pressure. As $t \to \infty$, formula (5) passes into the Langmuir isotherm written for absolute coverage.

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Note: Figure translations are in progress. See original paper for figures.

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