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Abstract

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PHYSICS

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ON THE SPECULAR REFLECTION OF VAPOR MOLECULES AND SUPRAMOLECULAR FLOW IN NARROW CAPILLARIES

The interaction of gas molecules with the surface of a solid may be characterized by a boundary transformant—the probability density for reflection of molecules in a definite direction with a definite velocity, for given direction and velocity of incidence (1). Its construction in the general case is a very complicated problem. Therefore, in practical calculations a specular-diffuse reflection scheme is used, representing the result of numerous experiments. The spatial distribution of reflected molecules in this case is determined by the cosine law, which has been confirmed by classical experiments (2,3). However, upon reflection of molecular beams from cleavage faces of alkali-halide crystals (4,5), a strong deviation from the cosine law is observed.

It was shown in (7) that some of the oxygen, nitrogen, and argon molecules are reflected specularly from optical glass and Teflon, with the fraction of specularly reflected molecules increasing as the angle of incidence increases.

On the basis of thermodynamic considerations, Epstein (6) showed that, at thermal equilibrium of the surface with the gaseous phase, the distribution of reflected molecules obeys the cosine law regardless of the quantitative ratio of specularly and diffusely reflected molecules. Here the concept of “reflected” molecules includes specularly reflected, inelastically scattered (diffusely reflected), and desorbed molecules. The conditions for the realization of specular and diffuse reflection are still unclear. It has been indicated, however, (5,8), that for specular reflection of a molecule to occur the following relation must be satisfied:

$$h \sin \alpha_0 < \lambda, \tag{1}$$

where h is the height of the irregularities on the surface of the solid, α_0 is a certain angle between the direction of motion of the incident molecule and the capillary wall at which specular reflection of all incident molecules occurs, and λ is the de Broglie wavelength of the incident molecules.

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Fig. 1. Schematic of the apparatus for measuring the evaporation rate of liquids from narrow capillaries into an atmosphere with various air pressures

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When molecules are reflected from cleavage faces of crystals, h is the amplitude of oscillations of atoms at the nodes of the crystal lattice.

J. K. Komsa $^{(9)}$ draws an analogy between the reflection of neutrons and molecules from the surface of a solid. Specular reflection occurs at a certain equipotential surface of the mean interaction potential. The limiting angle of total specular reflection is determined from the condition

$$\sin \alpha_0 = n, \tag{2}$$

where $n = \sqrt{1 - \frac{u}{E}}$ is the refractive index, determined in the same way as for neutrons, u is the potential energy of interaction of a molecule at the equipotential surface, and E is the kinetic energy of the molecule.

Motion of vapors in ultra-narrow capillaries. If the mean free path of vapor molecules $\bar{\lambda}$ is much greater than the diameter of the capillary, the flow is described by the well-known Knudsen equation. However, as was shown earlier, in capillaries with radii less than $0.1\,\mu$ the flux density of water vapor during evaporation into a vacuum is greater than that calculated from the Knudsen equation (^{10}).

If the vapor density and the diameter of the capillary are such that molecules reflected from the wall at an angle smaller than the limiting angle undergo the next collision with the wall without colliding with other molecules, then they will again be specularly reflected, and so on. If, in ordinary experiments on the study of the distribution of molecules reflected from a surface, specularly reflected molecules cannot be separated from diffusely reflected ones, then in our case there is, as it were, a separation of the stream of specularly reflected molecules from the total stream, since the former have a significantly greater transport mean free path and account for the main part of the gas flow. It was found that in freshly drawn capillaries, in the presence of an adsorption film, for water vapor $\alpha_0 = 5$–$7°$. For the vapor-flux density, theoretical calculations led to the expression:

Fig. 1. Schematic of the apparatus for measuring the evaporation rate of liquids from narrow capillaries into an atmosphere with various air pressures

$$i = \frac{\beta \bar{c}}{l} \ln \frac{p_0}{p}, \tag{3}$$

where i is the vapor-flux density, p_0, p are the vapor or gas pressures at the ends of the capillary, l is the length of the capillary, $\bar{c}$ is the mean molecular velocity, $\beta = \alpha_0^2 m / 2\sqrt{2}\pi\sigma^2$, m is the mass of a gas molecule, and σ is the molecular diameter.

The applicability of equation (3) was verified in (^{10}); however, it is desirable to give additional, still more direct evidence for the assumption that specularly reflected molecules influence the flux density. For this it is sufficient to show that, in the presence of a neutral gas, the flux density sharply decreases at a certain pressure of this gas, corresponding to the mean free path at which a molecule, after being reflected from the wall at an angle smaller than the limiting angle, collides with molecules of the other gas on average before its next collision with the wall.

Experimental procedure and results. The rate of evaporation of water from a capillary with a radius of $28\,\mu$ into an atmosphere with various air pressures was measured. The procedure for measuring the radii and for observing such capillaries is described in (^{11}). The capillary, sealed at one end and filled with water, was placed in a chamber (Fig. 1), where a prescribed air pressure was created by means of a fore-vacuum pump. To maintain the prescribed water-vapor pressure, silica gel was placed in the chamber. After the experiment, the amount of water contained in it was determined, and the vapor pressure was determined from the adsorption isotherm. The transition from the supramolecular regime to the molecular regime should occur at a mean free path $\bar{\lambda}$ of the order of

$$\bar{\lambda} = \frac{d}{\alpha_0},$$

where d is the capillary diameter and α_0 is the limiting angle of specular reflection in radians.

The experimental results are shown in Fig. 2 (for water, the evaporation rate is numerically equal to the vapor-flux density in the cross section of the capillary free from liquid).

The diameter of the capillary under study is smaller than the mean free path of air molecules even at atmospheric pressure. Consequently, the mechanism of vapor motion during the evaporation of water from such a capillary will be determined mainly by collisions of molecules with the walls, i.e., the Knudsen flow regime should be realized.

In Fig. 2, straight line 2 is constructed according to the Knudsen equation for the motion of water vapor with a pressure difference of 17.5 mm Hg, corresponding to the difference between the vapor pressure at the meniscus and in the surrounding atmosphere. As is seen from the figure, the presence of air has no effect on the rate of evaporation.

Fig. 2. Relation between the rate of evaporation of water and the reciprocal of the depth of the meniscus in a capillary $r = 28\,\mu$, $t = 20°$C (for water the rate of evaporation is numerically equal to the density of the vapor flux in the part of the capillary free of liquid). 1 –at 0-150 mm Hg. Straight line –according to equation (4). 2 –at 200-760 mm Hg. Straight line –according to the Knudsen equation. *a* –vacuum, *b* –150 mm, *v* –20 mm, *g* –60 mm, *d* –760 mm, *e* –200 mm Hg.

Fig. 3. Relation between the rate of evaporation of water and the reciprocal of the depth of the meniscus in a capillary $r = 0.028$ mm, $t = 10°$C. The straight line is constructed according to equations (8), (9), i.e., for the case when the elasticity of the vapor in the chamber is much less than the effusion pressure at the outlet from the capillary.

However, at lower air pressures in the chamber the rate of evaporation proves to be sharply increased and also does not depend on the air pressure in the chamber. Straight line 1 is constructed according to equation (3) for $\beta = 3 \cdot 10^{-10}$, $\alpha_0 = 5°$, $\sigma = 2.8$ Å.

From this one may draw the following conclusion. In sufficiently narrow capillaries there exists a narrow interval of air pressures in which the flow regime changes from Knudsen to supermolecular. The flux density determined by this regime likewise does not depend on the air pressure.

The realization of one or the other regime is determined by the conditions:

$$\text{for } 1 < \bar{\lambda}/d < 1/\alpha_0 \text{ –Knudsen flow,} \qquad (4)$$

$$\text{for } \bar{\lambda}/d > 1/\alpha_0 \text{ –supermolecular regime,} \qquad (5)$$

where α_0 is the limiting angle of specular reflection.

These conditions are approximate, because the specular-reflection regime begins at higher pressures (smaller mean free paths) than is determined by expression (2), since for molecules moving not in the planes of the central sections and describing a broken helical line, the distances between successive collisions with the walls will be smaller than for molecules moving in the plane of a central section. On the other hand, many molecules, being reflected at an angle smaller than α_0, and consequently their path will be much greater.

In the case under consideration, according to condition (5), specular reflection should have occurred at $\bar{\lambda} > 3.1 \cdot 10^{-5}$ cm ($p_a < 150$ mm Hg) and is in fact realized at $\bar{\lambda} > 2.5 \cdot 10^{-5}$ cm ($p_a = 200$ mm Hg), which is a satisfactory agreement.

At low vapor pressures in the surrounding atmosphere, equation (3) is inapplicable. In this case it is necessary to take into account the effusion jump at the outlet from the capillary channel. Thus, $p = p_e + p_1$ (p_e is the effusion jump, p_1 is the vapor pressure in the chamber).

The expression for the flux density takes the form

$$i = \frac{\beta \bar{c}}{l} \ln \frac{p_0}{p_e + p_1}. \tag{6}$$

The effusion jump is equal to

$$p_e = \frac{4RT}{\mu c} i. \tag{7}$$

Solving (6) and (7) together for the case $p_e \gg p_1$, we obtain

$$i = \frac{\beta \bar{c}}{l} u, \tag{8}$$

where u is found from the equation

$$ue^u = l\mu p_0 / 4\beta RT. \tag{9}$$

In Fig. 3 the straight line is plotted from equations (8), (9) for evaporation of water vapor into vacuum. $p_a = 3$ dyn/cm^2; $p_1 < 0.13$ dyn/cm^2; β, σ, λ, t have the values given above.

The agreement of the experimental points with the theoretical ones is satisfactory.

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