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On laser monitoring of transport processes in capillary porous bodies

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Abstract—Some trends in the diffusion of gases in capillaries exposed to resonance laser radiation are considered. The case of a free-molecular gas flow regime is studied in which the interactions of molecules with the walls of capillaries exert a substantial influence on the transport processes, the resonance radiation effect manifesting itself in the variation of such parameters as the energy and time of adsorption and the sticking probability. In fairly fine capillaries, when the surface transport of particles is significant, a change in the above parameters leads to the redistribution of the adsorbed phase density along the capillary length, as a result of which there appears a resultant flux of molecules even in the system previously in an equilibrium state. The problem of the radiation-induced drift of molecules in wide enough capillaries, when the transfer of particles over the surface may be neglected, is also considered. It is shown that radiation may cause a change in the course of the unsteady-state diffusion of gases in porous bodies.

1. INTRODUCTION

THE PRESENT-day technology is confronted with the pressing need for controlling the transport processes in different media. One of the most effective means of influencing the transport processes of gases is provided by laser radiation [1].

In the case of gas mixtures, the effect of resonance radiation on mass transfer is manifested in the difference between the collision cross-sections of the excited and nonexcited gas particles [2–4]. In the processes of gas motion in capillary-porous bodies, the transport phenomena are substantially influenced by the manner in which the particles interact with the walls of the pores, with the interaction of laser-excited gas particles differing considerably from that of nonexcited particles, which leads to different sticking probabilities for particles [5]. Laser radiation can also influence the adsorbed gas particles changing their time of adsorption and their surface diffusivity. Naturally, the transport processes are most appreciably influenced by the interaction of molecules with the wall under the conditions of free-molecular gas flow in body pores when the gasdynamic mean free path of particles exceeds the diameter of the pores. It is in this regime (or close to it) that a number of experiments have been carried out to study the effect of resonance laser radiation on gas diffusion in porous bodies.

In undertaking a theoretical analysis of the effect of resonance laser radiation on the flow of gases in isolated capillaries and porous bodies, it is necessary to distinguish two classes of problems. The first class includes problems dealing with the resultant mass flux on the walls of capillaries (i.e. the flux of particles sticking to the walls is in excess of the flux of evaporating particles). And when, in this case, the laser radiation influences the sticking coefficient of one of the mixture components, there appears the possibility for controlling the diffusion of gases in porous bodies and, consequently, the process of gas mixture separation [5–7]. The second class comprises problems in which the sink of particles in a porous body is absent, i.e. the number of particles sticking to the walls of capillaries is equal to those evaporating. Some of the problems dealing with the influence of laser radiation on rarefied gas flow in capillaries are considered in refs. [8–11].

It should be noted that in the problems of the first class the process is in principle an unsteady one, since with the passage of time the deposition of particles on the walls of capillaries will impair the permeability of a porous body to a gaseous phase till complete blocking of the pores. In contrast, in problems of the second class, the permeability of a porous body remains unchanged with time and a steady-state process of mass transfer is realized.

Based on the molecular-kinetic approach, the present work deals with the problems of the influence of laser radiation on transport processes in capillary-porous bodies under the conditions of free-molecular gas flow in capillaries in the absence of a resultant mass flux on the walls of capillaries (with no sink of particles in a porous body). The study is also concerned with the problems of the laser radiation-induced mass transfer in capillaries, the essence of which is that in the system, being previously in equilibrium, the mass fluxes start to originate on exposure to radiation.

2. THE EFFECT OF RESONANCE LASER RADIATION ON THE INTERACTION OF GAS PHASE PARTICLES WITH A SURFACE

Before starting a direct discussion of the effect of laser radiation on transport processes in porous bodies, it will be useful to briefly consider the possible effect of resonance radiation on the character of interactions of particles with a surface.

NOMENCLATURE

D_s coefficient of surface diffusion
h Planck constant
j_s density of the flux of molecules in the adsorbed phase
k Boltzmann constant
L capillary length
m mass of a molecule
n number density of molecules in the gas phase
n_a number density of adsorbed molecules
n_0 number density of molecules in a completely filled monolayer
P pressure
Q_a adsorption energy
Q_d energy of surface mobility activation
r capillary radius
T temperature
v mean velocity of molecules.

Greek symbols
α sticking probability
β coefficient of specular reflection
δ polymolecular film thickness
η dynamic viscosity
ν radiation frequency
ρ mass density of film substance
τ adsorption time.

A particle striking the surface may either reflect elastically from it or may for a while remain on the surface (be adsorbed). The sticking probability of the particle depends on whether or not the internal degrees of freedom of the falling particle have been excited. Thus, for example, for a vibrationally excited molecule the sticking coefficient can be expressed as [5]

$$\alpha = 1 - \exp\{-E_{sp}/E_g\}$$

where E_{sp} is the specific energy of gas molecule interaction with the surface depending on the ratio between the gas molecule and the adsorbent lattice atom masses and on the energy of adsorptional interaction. According to ref. [5], E_g is

$$E_g = E + E_v$$

where E is the energy of a nonexcited molecule and E_v is the energy of vibrational excitation.

The particles (molecules or atoms) adsorbed on the surface are characterized by the time of adsorption, τ, which can be expressed as [12]

$$\tau = \tau_0 \exp\left\{\frac{Q_a}{kT}\right\} \tag{1}$$

where τ_0 is the cycle of the adsorbed particle vibration in the direction normal to the surface.

In the majority of cases the particles, while being in the adsorbed state, participate in the surface diffusion process.

The surface diffusion coefficient has the form [12]

$$D_s = D_{s0} \exp\left\{-\frac{Q_d}{kT}\right\} \tag{2}$$

where Q_d is the activation energy of surface diffusion. According to ref. [13], the quantity $\phi = Q_d/Q_a$ varies usually in the range 0.1–0.8.

The particles adsorbed on the surface may either be desorbed from the surface, enter into chemical reaction or be absorbed.

Resonance laser radiation may exert a substantial influence on all of the above processes. This is due to both the usual radiative heating of a solid body and the change in the particle–surface interaction potential [14]. In view of the above, expressions (1) and (2) for τ and D_s in the presence of radiation can be written in the form [11]

$$\tau = \tau_0 \exp\left\{\frac{Q_a}{kT}(1-\Delta_1)\right\} \tag{3}$$

$$D_s = D_{s0} \exp\left\{-\frac{Q_d}{kT}(1-\Delta_2)\right\} \tag{4}$$

where

$$\Delta_1 = \frac{\Delta Q_a}{Q_a} + \frac{\Delta T}{T}, \quad \Delta_2 = \frac{\Delta Q_d}{Q_d} + \frac{\Delta T}{T}$$

with ΔQ_a and ΔQ_d characterizing the changes in the energy of adsorption, Q_a, and energy of activation of surface diffusion, Q_d, as a result of the resonance laser radiation effect on the system, ΔT is the change in the surface temperature due to radiative heating. It is assumed that $\Delta Q_d/Q_d$, $\Delta Q_a/Q_a$, $\Delta T/T \ll 1$ and that the factors in front of the exponentials remain constant.

The values of ΔQ and ΔT should, in principle, be determined from the solution of the problem on radiation interaction with a solid body in the presence of adsorbed particles on its surface and also of the problem of heat conduction in a solid body with account for radiation and energy liberation on adsorption of excited gas particles.

Note that, on resonance excitation of electron therms, the molecules can be transferred into the region of predissociation. When colliding with the surface, such excited molecules can dissociate into atoms. At the same time, the adsorption energy of molecules and of the constituent atoms may differ substantially. Respectively, the values of τ and D_s will also differ.

In the specular-diffuse scheme of the reflection of

molecules, which is usually employed in the kinetic theory of gases, it is assumed that a portion, f, of molecules is reflected in a diffuse manner and a portion, $1-f$, specularly. Frequently, it is not specified whether the first portion consists of elastically (but diffusely) reflected molecules or of the molecules desorbing from the surface. A more detailed analysis of the transport processes has shown that such a distinction should be made especially when investigating the resonance laser radiation effect on transport processes. Should the specular-diffuse scheme of interaction be interpreted to give that the molecules reflected specularly are those which reflect elastically and that the flux of molecules escaping the surface in a diffuse manner consists only of desorbing molecules, then the coefficient of specular reflection in this scheme will coincide with $1-\alpha$.

3. LASER RADIATION EFFECT ON RAREFIED GAS FLOW IN CAPILLARIES

For a free-molecular gas flow through a long cylindrical capillary of radius r, the flux of particles j, passing through the capillary cross-section, on the assumption of the diffuse reflection of particles from the walls, is [15]

$$j = -\tfrac{2}{3}\pi r^3 v \frac{\mathrm{d}n}{\mathrm{d}X} \tag{5}$$

where v is the mean velocity of molecules, and n is the number density of molecules in a gas phase.

The fact that the measured j exceeds the j predicted by formula (5) is usually explained either by the effect of specular reflections of particles from capillary walls, which is responsible for the factor $(2-f)/f$ in formula (5) [15], or by the surface diffusion transfer of adsorbed particles. In this latter case, an additional term, $-2\pi r D_s(\mathrm{d}n_a/\mathrm{d}X)$ [16], is introduced into formula (5).

In the real situation, both the specular reflections of particles from a capillary surface and the processes of adsorption and surface diffusion are likely to occur. Taking into account the fact that the surface diffusion process may involve only the particles adsorbed on the capillary walls and assuming the additivity of volumetric and surface fluxes and the validity of Henry's law for the process of adsorption, the quantity j for a steady-state case can be expressed as [17]

$$j = -\pi r^2\left(\frac{2-f}{f}\frac{2}{3}rv + \frac{\tau v\alpha}{2r}D_s\right)\frac{\mathrm{d}n}{\mathrm{d}X}. \tag{6}$$

When the particles which do not stick to the surface are reflected specularly, $f = \alpha$. For diffuse reflection, $f = 1$, but α may not be equal to unity.

In the case of specular reflections of nonsticking particles, equation (6) yields the following relation for the criterion which represents the ratio between the surface and volumetric fluxes of particles

$$G = \frac{3}{4}\frac{\tau D_s}{r^2}\left(\frac{\alpha^2}{2-\alpha}\right). \tag{7}$$

Since the values of α, τ, and D_s can vary in response to resonance laser radiation [5, 14], equations (6) and (7) imply that this influence can, in principle, be exploited to vary both the value of G and the total flux of particles transported through the capillary [17]. If the quantities τ_0, D_{s0}, ϕ, and α are supposed to be constant, then equations (3), (4), and (7) yield for the ratio of G_1 (without radiation) to G_2 (with radiation) the following expression

$$\frac{G_1}{G_2} = \exp\left\{(\Delta_1 - \phi\Delta_2)\frac{Q_a}{kT}\right\}.$$

For example, if $Q/k = 3000$ K, $T = 300$ K, $\phi = 0.2$, and $\Delta_1 = \Delta_2 = 0.1$, then $G_1/G_2 \approx 2.2$, i.e. the value of G has changed by more than a factor of two.

Taking into account equations (3) and (4) and the expression for the mean velocity, $v = (8kT/\pi m)^{1/2}$, the quantity j can be written as (assuming for simplicity that $f = 1$)

$$j = -T^{1/2}\left(A + \alpha B \exp\left\{\frac{Q_a(1-\phi)}{kT}\right\}\right)\frac{\mathrm{d}n}{\mathrm{d}X} \tag{8}$$

where

$$A = \tfrac{2}{3}r^3\left(\frac{8\pi k}{m}\right)^{1/2}, \quad B = \frac{\tau_0 D_{s0} r}{2}\left(\frac{8\pi k}{m}\right)^{1/2}.$$

Depending on the ratio between the terms in equation (8), the value of j can either increase or decrease with increasing T. The value of j also decreases with Q_a and α. Note that in the experiments carried out to study the effect of resonance laser radiation on the diffusion of gases in fine porosity bodies, a substantial reduction in the resultant flux on exposure to radiation has been revealed [18, 19].

Below, a brief description of the available published information concerning the influence of resonance laser radiation on the adsorption–desorption process, i.e. on the values of α, Q_a, and τ, is presented. According to ref. [5], the vibrational excitation of gas molecules reduces the sticking probability of molecules, i.e. the value of α. In ref. [20], a number of experimental works are surveyed, in which an increase in the rate of desorption in response to resonance laser radiation on the surface with adsorbed particles (corresponding to a decrease of τ) was observed. Theoretically, the mechanisms of laser-induced desorption were considered in ref. [14]. In refs. [21–23], the ideas are presented, according to which the polarizing effect of laser radiation increases the adsorption energy, Q_a, and respectively, the adsorption time, τ. And finally, in ref. [24], it is shown that laser radiation can either decrease or increase the interaction potential between the adsorbed particles and the semiconductor surface, depending on the sign of the particle charge. This, in turn, leads respectively to a decrease or an increase in the time of adsorption. Thus, the foregoing shows that the problem of the resonance laser radiation effect on the desorption process, i.e. on the values of Q_a and τ, is fairly involved and in each particular case should be solved with due account for

the specific properties of the adsorbent, adsorbate and acting radiation.

Note that equation (6) is written for an infinite capillary with fixed values of α, D_s, and τ along its length. This can be true for a capillary-porous body transparent to laser radiation. But there may take place another scheme of effect when laser radiation exerts an influence only on gas molecules at the body surface (the beam is parallel to the surface [5]). In this case, a portion of particles, entering the capillary on the side subjected to radiation, will be in the excited state. (In what follows, for the sake of definiteness, the case of vibrational excitation of molecules will be considered.) The portion of excited molecules, γ, may be found from the system of kinetic equations for the transitions of particles from the ground to the excited state (and inversely).

For a two-level model these equations have the form [7]

$$\frac{dn_1}{dt} = (n_2 - n_1)\frac{J\sigma}{h\nu} + \frac{n_2}{t_r} \tag{9}$$

$$\frac{dn_2}{dt} = (n_1 - n_2)\frac{J\sigma}{h\nu} - \frac{n_2}{t_r} \tag{10}$$

where n_2 and n_1 are the number densities of excited and nonexcited molecules, respectively, t_r is the time of collisional relaxation of molecules in a gas phase, J is the laser radiation intensity, and σ is the cross-section for resonance absorption.

The quantity γ is defined as $n_2/(n_1+n_2)$. In a steady state, it follows from equations (9) and (10) that

$$\gamma = \frac{J\sigma}{h\nu} t_r \Big/ \left(1 + 2\frac{J\sigma}{h\nu} t_r\right).$$

Evaluate now the value of the radiation-induced resultant flux of particles, passing through the capillary, in two cases: (1) when the transport is dominant in the adsorbed layer; and (2) when the transport predominates only in the gas phase. [The case at hand can be recognized with the aid of expression (7).] The densities of the molecular fluxes incident on the end surfaces of the capillary are supposed to be identical. On the assumption of the Maxwellian distribution function of the incident molecules, these are equal to $P/(2\pi mkT)^{1/2}$.

Furthermore, for the sake of simplicity, it is assumed that the sticking coefficient of nonexcited molecules is equal to unity, and of the excited molecules, to α. In the first case, when the transport predominates in the adsorbed layer, the following expression for the evaluation of j can be suggested, assuming that the particles sticking to the surface are nonexcited and that the values of D_s and τ are the same for both end surfaces of the capillary

$$j = \frac{2\pi r}{L}\frac{\gamma P \tau D_s}{(2\pi mkT)^{1/2}}(1-\alpha). \tag{11}$$

Note that in refs. [8, 9, 17] the quantity α was understood to be the averaged sticking coefficient of all the molecules entering the capillary from the zone exposed to radiation.

In the second case the flux of molecules passing through the capillary can be written as

$$j = \pi r^2 \frac{P}{(2\pi mkT)^{1/2}}(W_1 - W_2) \tag{12}$$

where W_1 and W_2 are the probabilities that a molecule will pass through a capillary in different directions.

Since the coefficient of vibrationally excited molecules differs from unity, then, in conformity with the above assumptions, the portion of specularly reflecting molecules, reaching the capillary from the laser-irradiated zone, will differ from zero. This results in the probability for a molecule to pass through a capillary, W_1, in the direction from the capillary mouth which faces the irradiated zone, being in excess of W_2, which is determined only by the diffuse distribution of molecules escaping from the wall [17].

Thus, in these two cases the laser induced mass fluxes have opposite directions. In the first case, with dominating transport over the surface, the flux of molecules will be directed into the radiation zone, since the mass transfer is governed by a drop in the concentration of adsorbed molecules, which is less on the capillary end surface facing the zone of laser radiation. In the second case, as shown above, the direction of mass flux is opposite. Note that mass transfer in capillaries also causes the transfer of energy. In addition to the energy of translational motion, the molecules will transfer the energy acquired as a result of laser excitation.

4. DETERMINATION OF THE PROBABILITY FOR THE PASSAGE OF MOLECULES THROUGH A CAPILLARY WITH LASER RADIATION TAKEN INTO ACCOUNT

Consider the problem of the influence of laser radiation on the probability for the passage of molecules through a capillary W [25], which is defined as the probability for the molecule, which has entered the capillary through its one end, to reach its other end with no allowance for its possible re-entry into the capillary after intermolecule collisions in the volume adjacent to the outlet section [26]. The conditions are assumed when the surface diffusion may be neglected.

The following expression can be written for W [26, 27]

$$W = 1 - \frac{2L}{r}\int_0^1 \frac{I}{N_0} K(x)\,dx \tag{13}$$

where x is the dimensionless coordinate ($x = X/L$), I is the density of the flux of molecules escaping from the capillary surface in a diffuse manner, N_0 is the density of the flux of molecules entering the capillary, K is the function characterizing the probability for the molecule escaping from the capillary wall to leave the capillary

through the section $x = 0$ without intermediate collisions with the wall.

It is assumed further that the relaxation of vibrational excitation follows the adsorptional mechanism, i.e. only the sticking (adsorbed) particles undergo relaxation with the sticking coefficient α being equal to $1-\beta$, where β is the portion of elastically (specularly) reflected molecules, and the sticking coefficient of nonexcited molecules being equal to unity. Then, the equation for I can be written as

$$I = \gamma(1-\beta)^2 N_0 M(x) + (1-\gamma)N_0 K(x) + \int_0^1 I K_1(|x-x'|)\,dx'. \quad (14)$$

Here $M(x)$ is the function characterizing the probability for a molecule to hit a surface element in the vicinity of point x with intermediate reflections taken into account [27]

$$M(x) = K(x) + \sum_{n=2}^{\infty} \beta^{n-1} K\left(\frac{x}{n}\right).$$

The function $K_1(x)$ is related to $K(x)$ by

$$K_1(x) = -\frac{dK(x)}{dx}.$$

Suppose that $\beta \ll 1$. The solution for I will be sought in the form of a series in the small parameter

$$I = I_0 + \beta I_1 + \beta^2 I_2 + \dots \quad (15)$$

In what follows, only the first two terms in equation (15) will be used.

Substituting expression (15) into equation (14), equating the terms with identical powers of β, and using the exponential approximation of $K(x)$, $K_1(x)$ [28] yields the following equations for I_0 and I_1

$$I_0 = \tfrac{1}{2}\exp\{-xl\}N_0 + \frac{l}{2}\int_0^1 I_0 \exp\{-l(|x-x'|)\}\,dx'$$

$$I_1 = -\gamma N_0 \exp\{-xl\} + \tfrac{1}{2}\gamma N_0 \exp\left\{-\frac{xl}{2}\right\} + \frac{l}{2}\int_0^1 I_1 \exp\{-l|x-x'|\}\,dx'$$

the solution of which has the form

$$I_0 = A + Bx \quad (16)$$

$$I_1 = \gamma(A+Bx) + \frac{\gamma N_0}{2+l}\exp\left\{-\frac{l}{2}\right\}(1+lx) - \tfrac{3}{2}\gamma N_0 \exp\left\{-\frac{xl}{2}\right\} \quad (17)$$

where

$$A = N_0\frac{1+l}{2+l}; \quad B = -\frac{N_0 l}{2+l}; \quad l = \frac{L}{r}.$$

With equations (15)–(17) taken into account, the ratio W/W_0, where W_0 is the probability for a molecule to pass through a capillary without being irradiated, is

$$W/W_0 = 1 + \beta\gamma\left(1 - \exp\left\{-\frac{l}{2}\right\}\right). \quad (18)$$

It is seen from equation (18) that the probability for a molecule to pass through a capillary in the presence of specular reflections ($\beta \neq 0$) will be higher than in the case of purely diffuse reflection ($\beta = 0$).

Note that in the case of irradiation of a capillary-porous body which is transparent to radiation, the probability for laser-excited molecules to pass through a capillary can be also increased as a result of the Doppler effect [25, 29]. Let the radiation frequency be somewhat smaller than the frequency of molecule transitions to the excited state. Then, due to the Doppler effect, the radiation will excite the molecules which move in the opposite direction of the radiation flux [2–4]. The probability of elastic reflection, which, as mentioned above, is considered to be specular, of vibrationally excited molecules will be higher than of nonexcited ones. Thus, a greater portion of excited molecules (the probability of specular reflection of which is higher) will enter the side opposite to the direction of radiation. Moreover, the molecules desorbing from the surface (nonexcited), when moving along the capillary opposite to the direction of radiant flux, can also, with a certain probability, be excited and reflected specularly from the wall. The molecules travelling with the radiation flux will be not excited (consequently, the probability of their specular reflection will be smaller). Thus, with equal fluxes of molecules incident on a porous body from both sides, a greater portion of molecules will be transferred through the body in the direction opposite to that of the radiant flux. The equation for the quantity I can be written in this case in the form [29]

$$I = \gamma(1-\beta)^2 N_0 M(x) + (1-\gamma)N_0 K(x) + \gamma_1(1-\beta)\int_0^x I M_1(x-x')\,dx' + (1-\gamma_1)\int_0^x I K_1(x-x')\,dx' + \int_x^1 I K_1(x'-x)\,dx'$$

where γ_1 is the probability of molecule excitation during its motion from one surface element of the capillary to another

$$M_1(x) = K_1(x) + \sum_{n=2}^{\infty} \frac{\beta^{n-1}}{n} K_1\left(\frac{x}{n}\right).$$

Note that the values of γ and γ_1 are assumed to be averaged over the directions and velocities of particles.

The analysis of the quantity W/W_0 has shown that it increases with the parameters l, β, γ, and γ_1.

In the case of the slip regime of gas flow, the effect of resonance laser radiation on mass transfer will be accounted for by the gas slip term [11], the value of

which depends on the nature of the gas flow in the Knudsen layer. It is clear that in this case too one will observe the above-mentioned effects which were observed for the free-molecular gas flow on a change in β.

5. LASER RADIATION INFLUENCE ON MASS TRANSFER IN A CAPILLARY WITH REGARD FOR SURFACE DIFFUSION

Consider in more detail the problem of mass transfer in capillaries with the surface diffusion taken into account and on the assumption of diffuse distribution of molecules escaping from the capillary surface (either desorbing or elastically reflecting) [8–10, 30]. Note that the expressions for j, given in Section 3, are valid only for long enough capillaries. Relation (6) has been obtained on the assumption of local equilibrium between the volumetric vapour phase and the adsorbed layer in each section of the capillary, which is not always reasonably correct, since then the correlation between the transport processes on the inner and end capillary surfaces (end effects) are not taken into account. The end effects will be especially important in those cases when radiation exerts an influence on the molecules in both the gas and adsorption phases from one side of a porous body which is not transparent to laser radiation.

First, consider the case when laser radiation influences the molecules in a gas phase (the beam is parallel to the end surface of the capillary). As mentioned earlier, in this case the selective effect of radiation on the transport processes is based on the difference between the interactions of excited and nonexcited molecules with the surface, namely, on the difference between their sticking probabilities.

The classification into two schemes, i.e. when radiation exerts an influence on the molecules in the gas phase (the beam is parallel to the surface) and when it influences the particles in the adsorbed state (the beam is incident on the surface), is, of course, a matter of convention. It should be noted that a laser beam incident on a surface may, naturally, excite the molecules in the gas phase also. On the other hand, when the beam influences the gas near the surface, heat can be generated due to the deactivation of the excited molecules on the surface and, as a consequence, due to a change in the time of adsorption and in the surface diffusion coefficient. However, in order to better understand the mechanism of mass transfer, it seems expedient to analyse a separate effect of various factors.

Analyse in more detail the model problem considered in Section 3. As earlier, assume that a portion, γ, of molecules that enter the capillary from the laser radiated region is excited and is characterized by the sticking coefficient α; the molecules entering the capillary at $x = 0$ are not excited and have a sticking coefficient equal to 1. Further assume that the time of vibrational relaxation of molecules adsorbed on the surface is much smaller than the mean adsorption time, so that the molecules desorbed from the surface are not excited either. The probabilities of vibrational relaxation (without sticking) during molecule collision with a clean surface and with an adsorption layer are supposed, for the sake of simplicity, to be equal to zero. The case when these quantities differ from zero is considered in ref. [30].

It is known that in fine enough capillaries the mass is transferred both in the gas phase and via surface diffusion.

In deriving equations to describe the degree of filling of the inner capillary surface with adsorbed molecules, θ, use is made of the assumption of the Langmuir monomolecular adsorption theory, which postulates that the molecules falling on the surface regions, occupied by adsorbed molecules, are reflected back into the gas phase. However, in contrast to the common assumption that all the molecules, falling on the surface regions which have not been occupied by the adsorbed molecules, are adsorbed, here the possibility of their elastic reflection is inferred in conformity with what has been said above.

The continuity equation for an adsorbed layer element in a steady-state case is

$$-\operatorname{div} j_s = I_d - \alpha_i(1-\theta)I^- \tag{19}$$

where I_d is the flux of molecules desorbed from the unit surface of the channel, and I^- is the flux of molecules incident per unit surface. According to Section 2, the value of α_i in equation (19) depends on whether the molecules, which fall on the surface, are excited or not. The quantities j_s and I_d are defined as

$$j_s = -D_s n_0 \frac{d\theta}{dX}, \quad I_d = \frac{n_0\theta}{\tau}. \tag{20}$$

Using expressions (19) and (20) and taking into account the above assumptions, the following system of equations is obtained to determine the coverage of the surface with adsorbed molecules

$$\frac{n_0}{L^2}\frac{d}{dx}\left(D_s\frac{d\theta}{dx}\right) = \frac{n_0\theta}{\tau} - (1-\theta) \times \left[\int_0^1 \left(I_2 + \frac{n_0\theta}{\tau}\right)K_1(|x-x'|)\,dx' + N_0K(x) + (1-\gamma)N_1K(1-x)\right] - (1-\theta)\alpha\left[\int_0^1 I_1K_1(|x-x'|)\,dx' + \gamma N_1K(1-x)\right] \tag{21}$$

$$I_1 = [1-\alpha(1-\theta)]\left[\int_0^1 I_1K_1(|x-x'|)\,dx' + \gamma N_1K(1-x)\right] \tag{22}$$

$$I_2 = \theta\left[\int_0^1 \left(I_2 + \frac{n_0\theta}{\tau}\right)K_1(|x-x'|)\,dx' + N_0K(x) + (1-\gamma)N_1K(1-x)\right] \tag{23}$$

where I_1 and I_2 are the flux densities of elastically reflected excited and nonexcited particles.

The meaning of separate terms in equations (21)–(23) will become evident from the analysis of equation (22). The first term in square brackets expresses the probability for a molecule falling on the surface to be reflected from it elastically. The second term in square brackets characterizes the flux of excited particles falling on this surface element. This flux consists of the particles escaping from the inner surface of the capillary and those entering it through the capillary mouth.

For the end surfaces of the capillary, the following boundary conditions may be written

$$\left.\frac{d\theta}{dx}\right|_{x=0} = \frac{L}{\sqrt{(D_s\tau)}}[\theta(0)-\theta_{0e}],$$

$$\left.\frac{d\theta}{dx}\right|_{x=1} = \frac{L}{\sqrt{(D_s\tau)}}[\theta_{1e}-\theta(1)]$$

where

$$\theta_{0e} = \frac{N_0\tau}{n_0+N_0\tau}, \quad \theta_{1e} = \frac{\alpha N_1\tau\gamma+(1-\gamma)N_1\tau}{n_0+\alpha N_1\tau\gamma+(1-\gamma)N_1\tau}.$$

The total flux of molecules, escaping from the capillary through the cross-section $x = 1$, consists of the molecules passing through the capillary without colliding with the walls, those leaving it through the cross-section after desorption or after elastic reflection from the walls and of a surface flux of molecules, i.e.

$$j_r = \pi r^2\left[N_0K_2(1)+2l\int_0^1\left(\frac{n_0\theta}{\tau}+I_1+I_2\right)\times K(1-x)\,dx\right]-\frac{2\pi r}{L}D_sn_0\left.\frac{d\theta}{dx}\right|_{x=1}$$

where $dK_2/dx = -2lK$.

As noted above, in order to simplify the analysis, it was assumed in refs. [9, 10] that all the molecules entering a capillary from the laser-irradiated side are characterized by some mean sticking coefficient, $\bar{\alpha}$, which differs from the sticking coefficient of nonexcited molecules, which was supposed to be equal to unity. For the case of $\theta \ll 1$, an approximate analytical solution for the system of equations has been obtained. The problem of mass transfer initiation in a capillary at equal effusion potentials on its ends has been analysed. The quantity $\varepsilon = (j_r-\pi r^2N_0)/\pi r^2N_0$ has been calculated which characterizes the influence of a change in the sticking coefficient on mass transfer initiation in a capillary. The calculations show that the value of ε decreases with an increase of r and $\bar{\alpha}$. Thus, for example, at $L = 10^{-7}$ m, $D_s = 10^{-9}$ m^2 s^{-1}, $\tau = 10^{-5}$ s, $r = 10^{-8}$ m, $\varepsilon \approx 1.3$ and 3 for $\bar{\alpha} = 0.8$ and 0.55, respectively.

In the case of a mixture of gases moving through a capillary, when, under the conditions specified above, each species is transferred by itself, the quantity ε can be used to characterize the effect of mixture separation at the capillary outlet. Since the values of ε depend, in principle, on which of the components is laser-excited, this provides the possibility for the selective separation of mixtures [10]. The problem of mass transfer induction in a capillary with a variable time of adsorption was considered in ref. [8]. The adsorption times may vary in response to laser-irradiation of an adsorbent–adsorbant system both as a result of the effect on the adsorbed particles [14] and as a result of the effect on the adsorbent surface leading to the redistribution of the electron density and to a change of the potential of the adsorbed particle interaction with the surface [24]. Naturally, the value of τ will also vary as a result of the usual heating of the body.

6. LASER RADIATION EFFECT ON POLYMOLECULAR FILMS IN CAPILLARIES

Consider now the problem of the laser radiation effect on polymolecular film flow in a capillary. Let the pressure P_1 and P_2 at the capillary mouths be maintained close to the saturation pressure P_e. Taking into account the fact that not all of the molecules falling on the surface of the condensed phase stick to it, it is possible to obtain the following system of equations for the distribution of polymolecular layer thickness (just as in the case of a monolayer the desorbing and elastically reflecting molecules are considered to escape from the surface by cosine law) [11, 31]

$$\frac{\rho A}{\eta mL^2}\frac{d}{dx}\left(\delta^{-1}\frac{d\delta}{dx}\right) = j_f-\alpha \times\left[\int_0^1(j_f+I)K_1(|x-x'|)\,dx'+N_0K(x)+N_1K(1-x)\right] \tag{24}$$

$$I = (1-\alpha)\left[\int_0^1(j_f+I)K_1(|x-x'|)\,dx' + N_0K(x)+N_1K(1-x)\right] \tag{25}$$

where A is the parameter which characterizes the interaction between the film molecules and a substrate. The quantity j_f is the flux of molecules evaporating from the film, which can be expressed as

$$j_f = n_f\left(\frac{kT}{2\pi m}\right)^{1/2}\exp\left\{-\frac{1}{kT}\left(Q+\frac{A}{\delta^3}\frac{m}{\rho}\right)\right\} \tag{26}$$

where n_f is the number density of molecules in the film and the second term in the exponential function characterizes a change in the film evaporation heat as compared with the evaporation heat Q of the massive material.

The term on the LHS of equation (24) describes the flow of a polymolecular film. In the case of a small value of the parameter $\rho A/\eta mL^2$, the differential term in equation (24) will influence the film profile only within narrow boundary layers at the capillary ends and can be neglected when evaluating the adsorption capacity of the capillary. In view of the above, equations (24) and (25), with the exponential approximation of K, K_1 for

the quantity $\delta(x)$, yields [11, 31]

$$\delta(x) = \left(\frac{Am}{\rho kT \ln [j_0/\alpha(A' + B'x)]}\right)^{1/3} \quad (27)$$

where

$$j_0 = n_f\left(\frac{kT}{2\pi m}\right)^{1/2} \exp\left\{-\frac{Q}{kT}\right\}$$

and A' and B' are determined as

$$A' = N_0\frac{l+1}{l+2} + N_1\frac{1}{l+2}, \quad B' = (N_1 - N_0)\frac{l}{l+2}.$$

As can be seen from equation (27), with a decreasing α the thickness of the polymolecular film decreases. Moreover, in addition to influencing the value of α, laser radiation may also exert an influence on the exponent in equation (26) (decrease it), which also leads to a decrease in the film thickness. The flow of mass transferred in a polymolecular film has the form [32]

$$j_m = 2\pi r\frac{\rho\delta^3}{3\eta}\frac{d(A/\delta^3)}{dX}. \quad (28)$$

From what has been said and from equation (28) it follows that the radiation effect on a polymolecular film can initiate the flow of the latter through a capillary at $N_0 = N_1$ in the case when radiation causes the above quantities to be dependent on coordinates.

7. THE INFLUENCE OF LASER RADIATION ON THE EFFECTIVE DIFFUSION COEFFICIENT IN THE CASE OF UNSTEADY-STATE GAS DIFFUSION IN A POROUS BODY

Consider in brief the problem of the resonance laser radiation effect on the process of unsteady-state diffusion in porous bodies. As is noted in ref. [25], in the case of unsteady-state diffusion the radiation may bring about a change in the effective diffusion coefficient, which for the dusty gas model, neglecting surface diffusion, can be written as

$$D = \frac{1}{3}\frac{\lambda_2^2}{\lambda_2/v + \alpha\tau}\frac{\lambda_1}{\lambda_1 + \lambda_2} \quad (29)$$

where λ_1 and λ_2 are the gasdynamic mean free path of particles and mean free path of particles relative to the particles modelling the skeleton of a porous body, respectively.

Taking into account the fact that for free-molecular flow along a cylindrical capillary $\lambda_2 = 2r$ and $\lambda_1 \gg \lambda_2$ at $\alpha = 1$, it is possible to show that equation (29) coincides with the well-known expression for the effective diffusion coefficient in a cylindrical capillary [33]

$$D = \frac{4}{3}\frac{r^2}{2r/v + \tau}.$$

It follows from equation (29) that a radiation-induced change in the values of α and τ is accompanied by a change in the effective diffusion coefficient D. A similar expression is also used in refs. [22, 23] to interpret the experimental results on the effect of laser radiation on the diffusion of gases in relatively wide capillaries (about 10^{-4} m in diameter), when the surface diffusion of adsorbed molecules may be neglected. However, as noted in ref. [34], in the steady-state case under the conditions specified, the flux of particles depends only on the mobility and number of particles being in a gaseous state, and is independent of the adsorption process, i.e. of the quantities α and τ, and, consequently, of the adsorption energy Q_a. This can also be shown by the method considered in Section 5.

For capillaries of small enough radii, the effective diffusion coefficient at $\alpha = 1$ is [12]

$$D = \frac{\frac{4}{3}r^2 + D_s\tau}{2r/v + \tau}.$$

Note that the characteristic time for the process to become a steady-state one, which can be evaluated as equal to $t_c \sim L^2/D$, depends considerably on the radii of capillaries. Thus, for example, for $L = 5 \times 10^{-2}$ m, $\tau = 10^{-6}$ s, $D_s = 10^{-9}$ m^2 s^{-1}, $v = 300$ m s^{-1} and $r = 5 \times 10^{-9}$ m one obtains $t_c \sim 10^6$ s and at $r = 10^{-4}$ m and the same remainder parameters, $t_c \sim 10^{-1}$ s. It is evident that for the fine porosity bodies and for bodies with relatively wide capillaries the times required to attain a steady-state regime differ substantially.

8. CONCLUSION

A specific aspect of the control of transport processes in capillary-porous bodies is associated with the fact that in passing through a porous body a molecule experiences multiple collisions with the walls of the pores. If, in this case, the interactions of a laser-excited molecule and of a nonexcited molecule with the wall differ, there arises the possibility to control the transport processes by means of resonance laser radiation.

The present analysis has shown that resonance laser radiation may induce the fluxes of particles in the system being previously in the state of equilibrium, i.e. light-induced drift of particles. This phenomenon is attributed to a radiation-induced change in such parameters as the energy and time of adsorption and the sticking coefficient. In fine porosity bodies, mass transfer initiation is brought about by the motion of particles in the adsorbed phase. In wide enough capillaries, when substance transfer in the adsorbed phase may be neglected, the laser-induced mass (and energy) transfer may occur as a result of the change in the trajectories of the excited particles in a capillary. For example, in the scheme of diffuse-specular reflection of particles, it is revealed in the difference between the probabilities of specular reflection of the excited and nonexcited particles.

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SUR LE PILOTAGE PAR LASER DES MECANISMES DE TRANSPORT DANS LES CORPS POREUX CAPILLAIRES

Résumé—On considère quelques allures de la diffusion des gaz dans des capillaires exposés au rayonnement laser en résonance. On étudie le cas du régime d'écoulement moléculaire libre pour lequel les interactions des molécules avec la paroi des capillaires exercent une influence sensible sur les mécanismes de transport ; l'effet de résonance du rayonnement introduit une variation de paramètres comme l'énergie et le temps d'adsorption et la probabilité d'accrochage. Dans des capillaires très fins, quand le transport surfacique des particules est sensible, un changement des paramètres précédents conduit à une redistribution de la densité de phase adsorbée selon la longueur capillaire, comme s'il apparaissait un flux résultant de molécules même dans le système initialement à l'état d'équilibre. Le problème de la poussée des molécules induite par le rayonnement dans les capillaires assez larges est considéré quand le transfert des particules sur la surface peut être négligé. On montre que le rayonnement peut provoquer un changement dans la diffusion instationnaire des gaz dans les corps poreux.

ÜBER DIE BEOBACHTUNG VON TRANSPORTPROZESSEN IN KAPILLAREN PORÖSEN STOFFEN MIT HILFE VON LASERSTRAHLEN

Zusammenfassung—Einige Vorgänge der Gasdiffusion in Kapillaren unter dem Einfluß von Laserresonanz werden betrachtet. Der Fall einer freien molekularen Gasströmung, in der die Wechselwirkung von Wänden und Molekülen die Transportprozesse wesentlich beeinflussen, wird untersucht. Der Resonanzeffekt der Strahlung äußert sich dabei in der Änderung von Größen wie der Energie und der Zeitdauer der Adsorption und der Aufenthaltswahrscheinlichkeit. In sehr dünnen Kapillaren, wo der Oberflächentransport der Teilchen wesentlich ist, führt eine Änderung der obengenannten Parameter zu einer Neuverteilung der Dichte der adsorbierten Phase längs der Kapillare. Daraus ergibt sich ein resultierender Strom von Molekülen selbst in einem System, das sich vorher im Gleichgewicht befand. Das Problem der strahlungsinduzierten Drift der Moleküle in weiten Kapillaren, in denen der Teilchentransport an der Oberfläche vernachlässigt werden kann, wird auch betrachtet. Es wird gezeigt, daß Strahlung eine Änderung des Verlaufs der instationären Gasdiffusion in porösen Körpern hervorrufen kann.

ОБ УПРАВЛЕНИИ ПРОЦЕССАМИ ПЕРЕНОСА В КАПИЛЛЯРНОПОРИСТЫХ ТЕЛАХ С ПОМОЩЬЮ ЛАЗЕРНОГО ИЗЛУЧЕНИЯ

Аннотация—Рассмотрены некоторые закономерности диффузии газов в капиллярах с учетом воздействия резонансного лазерного излучения. Исследован случай свободномолекулярного режима течения газа, при котором существенное влияние на явления переноса оказывают процессы взаимодействия молекул со стенками капилляров. При этом влияние резонансного излучения проявляется в изменении таких параметров, как энергия адсорбции, время адсорбции, коэффициент прилипания. В достаточно узких капиллярах, когда существенен поверхностный перенос частиц, изменение указанных величин приводит к перераспределению плотности адсорбированной фазы по длине капилляра, в результате чего появляется результирующий поток молекул даже в случае, когда до включения излучения система находилась в равновесии. Рассмотрен также вопрос об индуцированном излучением дрейфе молекул в достаточно широких капиллярах, когда переносом частиц по поверхности можно пренебречь. Показано, что при воздействии излучения может измениться ход нестационарного процесса диффузии газа в пористых телах.