CALCULATION OF THE GAS DIFFUSION COEFFICIENT IN MICROCAPILLARIES

USING MOLECULAR DATA

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An expression is obtained for calculation of the diffusion coefficient of rarefied gases in microcapillaries with consideration of the action of the surface force field.

On the basis of the molecular-statistical approach, it has been proposed [1] that the diffusion coefficient for a rarefied gas (i.e., a gas whose particles do not interact with each other) within a microcapillary and the adsorption field of the capillary walls can be defined as the mean square of the gas molecule displacement $\rho(\tau)$ over an interval τ:

$$D \quad \rho(\tau)/\tau, \tag{1}$$

where

$$\rho(\tau) \quad \frac{1}{2} \langle (\mathbf{r}(t+\tau) - \mathbf{r}(t))^2 \rangle = \frac{1}{2} \langle \Delta r^2(\tau) \rangle,$$

where r(t) is the displacement of a molecule over time t. The values in angle brackets indicate averages over time. Using the ergodic hypothesis, in the future we will calculate mean values where required by the Gibbs method.

The essence of the molecular-statistical approach is that the macroscopic characteristics of the system can be related to mean values of quantities related to individual molecules. Thus, for example, temperature T is defined as the mean energy of molecular motion, $m\langle v^2\rangle/2=3kT/2$. We will use such an approach to study diffusion of a rarefied gas in an infinite microcapillary, which for definiteness we will assume cylindrical with radius r_c (Fig. 1).

We will turn to consideration of the microscopic pattern of gas molecule motion. Being located in the vicinity of atoms within the lattice of the capillary wall, which perform thermal oscillations about their equilibrium positions, the gas molecule exchanges energy with the wall atoms, which establishes an equilibrium Maxwell distribution over velocities. The kinetic energy of a gas molecule is equal to $m\langle v^2\rangle/2$. In the absence of capillary walls, the molecular motion is chaotic, i.e., equiprobable in all directions, but the field of the surface forces changes the character of the motion. The interaction of each gas molecule with each molecule of the capillary wall, the two being separated by a distance r, may be specified, for example, by a (6-12) Lennard-Jones pair potential with parameters ϵ, σ:

$$u(r) \quad 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]. \tag{2}$$

The potential field within the capillary U can then be obtained by integrating air interactions u(r) over all capillary wall atoms. In view of the fact that the capillary is infinite and cylindrical symmetry will be in effect, the potential U(R), and thus, the force $F(R) = -\mathrm{grad}\, U(R)$ will be functions of the single variable R, the distance of the gas molecule from the capillary axis. The form of the potential U(R) for the system studied was obtained in the approximation of the capillary walls being a continuous medium in [2]. In the surface force field created by the walls there will act upon a gas molecule a mean force $\langle |F| \rangle$, which by definition (by Gibbs averaging) will equal:
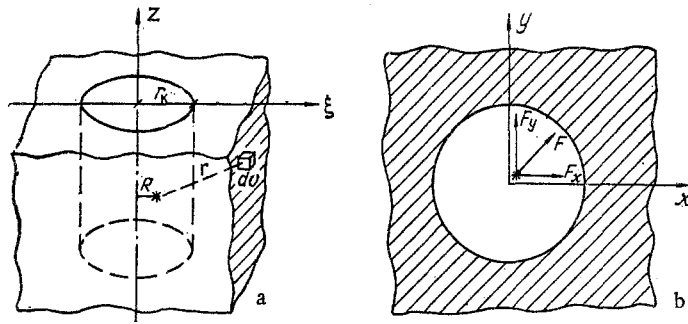
Fig. 1. Diagram of infinite capillary of radius r_c; * represents a diffusing gas molecule.

$$\langle F \rangle \equiv \frac{\int\limits_0^{r_h} F(R) \exp[-U(R)/kT]\, dR}{\int\limits_0^{r_h} \exp[-U(R)/kT]\, dR}.$$

It is clear that under the influence of the wall field the diffusion coefficient D will vary and depend on $\langle |F| \rangle$. It should be noted that the mean over time of gas molecule displacement along the capillary axis is equal to zero, but the mean square of the displacement, on which D is dependent, is not equal to zero.

The problem of calculating the diffusion coefficient from molecule data, according to Eq. (1), reduces to finding $\rho(\tau)$ and defining the system characteristic time τ_0. From physical considerations, for τ_0 we may take the time corresponding to change in the direction of a molecule's motion due to interaction with the wall. To determine this we turn to the well-known linear response theory of [3], which is widely used in statistical thermodynamics. According to this theory the diffusion coefficient can be expressed in terms of the velocity autocorrelation function $A(\tau)$:

$$D = \int\limits_0^\infty \langle \mathbf{v}(t+\tau)\cdot\mathbf{v}(t) \rangle\, d\tau \equiv \int\limits_0^\infty A(\tau)\, d\tau. \tag{3}$$

Application of the generalized virial theorem

$$\langle \mathbf{r}^{(i)}(t)\cdot r^{(i+n)}(t) \rangle = \begin{cases} 0 & \text{if } n \text{ is odd,} \\ (-1)^\kappa \langle r^{(i+\kappa)^2}(t) \rangle, & \text{if } n = 2\kappa\,(\kappa = 1,\,2,\,\ldots) \end{cases}$$

to expansions in a Taylor series in powers of τ of the correlators $\mathbf{v}(t+\tau)\cdot\mathbf{v}(t)$ and $(\mathbf{r}(t+\tau)-\mathbf{r}(t))^2$ gives [4]

$$A(\tau) = \sum_{i=0}^\infty \frac{(-1)^i \tau^{2i}}{(2i)!} \langle v^{(i)^2}(t) \rangle = \langle v^2 \rangle - \frac{1}{2m^2} \langle F^2 \rangle \tau^2 + \frac{1}{24m^2} \langle F^{(1)^2} \rangle \tau^4 - \ldots, \tag{4}$$

$$\rho(\tau) = \sum_{i=0}^\infty \frac{(-1)^i \tau^{2i+2}}{(2i+2)!} \langle r^{(i+1)^2}(t) \rangle, \tag{5}$$

where $v^{(i)}(t)$ and $r^{(i)}(t)$ are the i-th derivatives with respect to time of the molecular velocity and displacement. As is evident from expansions (4), (5), $A(\tau)$ and $\rho(\tau)$ are functions of the mean square of the force $\langle F^2 \rangle$ and its derivatives.

In the study of **mass-transfer** phenomena one is usually interested in the longitudinal component of the diffusion coefficient D_z, along the capillary axis. This simplifies the problem, since in this case in Eq. (1) the longitudinal component $\rho_z(\tau)$ appears. Since in the longitudinal direction the force and its derivatives are equal to zero $\left(F_z = -\dfrac{\partial U}{\partial z} = 0 \right)$,

in Eq. (5) only the first term $\langle v_z^2 \rangle \tau^2/2$ will be nonzero.
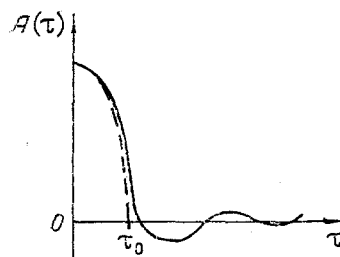
Fig. 2. Form of autocorre-
lation function A(τ) for
diffusing gas molecule.

To make an estimate of τ_0 we will use the following assumptions: a) gas molecule dif-
fusion in the strong adsorption field of the capillary walls is similar to particle motion
in dense gases and condensed media, in the sense that in very narrow pores the distance be-
tween a gas molecule and the wall will be of the same order of magnitude as the intermolecu-
lar distances in such systems; b) the autocorrelation function of the gas molecule velocity
in the adsorption field has an oscillating form, or at least one zero value, corresponding
to a change in the sign of molecular velocity, i.e., a turning point; the characteristic
form of the function A(τ) is shown in Fig. 2; c) in the system under consideration the char-
acteristic time interval is the time τ_0, which defines the transverse force, since inter-
action with the walls is the only cause of change in the direction of molecular motion.

Commencing from point b), to determine τ_0 we use expansion (4), limiting ourselves to
the first two terms, which is equivalent to a parabolic approximation of the function A(τ)
(the dashed curve of Fig. 2) to find the smallest root A(τ) = 0. The τ_0 value obtained in
this manner is smaller than the true value of the root. Then expansion (4), according to
point c), must be considered in a plane perpendicular to the capillary axis. We will con-
sider expansion (4) for the system under study in a plane (x, y), perpendicular to the
capillary axis, with origin on the axis (Fig. 1b):

$$\langle v_x^2 + v_y^2 \rangle - \frac{1}{2m^2} \langle F_x^2 + F_y^2 \rangle \tau^2 = 0. \tag{6}$$

Inasmuch as $\langle v_x^2 + v_y^2 \rangle = 2kT/m$, while $\langle F_x^2 + F_y^2 \rangle = \langle \left(\frac{\partial U}{\partial R} \right)^2 \rangle \equiv \langle F^2 \rangle$, we obtain from Eq. (6)

$$\tau_0 \simeq \sqrt{\frac{4kTm}{\langle \left(\frac{\partial U}{\partial R} \right)^2 \rangle}} = \sqrt{\frac{4kTm}{\langle F^2 \rangle}} . \tag{7}$$

Substituting $\rho_z(\tau) = \langle v_z^2 \rangle \tau_0^2/2$ and Eq. (7) in Eq. (1), we have

$$D_z \simeq \frac{(kT)^{3/2}}{\sqrt{m \langle F^2 \rangle}} . \tag{8}$$

Applying the tools of differential geometry [5], we can write an equation relating the
square of the force to the trajectory parameters, i.e., the curvature $\varkappa$ and the change in
kinetic energy K along the arc trajectory s:

$$(F(R))^2 = \left(\frac{dK}{ds} \right)^2 + 4K^2\varkappa^2. \tag{9}$$

From this we have a simple kinematic image: the values of $(F(R))^2$ in Eq. (9) characterize
the changes in molecular velocity along the trajectory and the change in trajectory curva-
ture under the action of the surface force field. The greater the force acting, the more
curved is the trajectory and the more it deviates from linearity, thus leading to reduction
of the diffusion coefficient.

Consideration of a concrete problem — diffusion of rarefield gas molecules (with $\lambda \geqslant$
r_c, where λ is the free path length) in infinite microcapillaries with the aid of Eq. (8)
has allowed derivation of the principles of D_z behavior with change in temperature T and
capillary radius r_c. It develops that in the capillary wall adsorption field D_z is propor-

tional to T in the range of temperatures comparable to the depth of the intermolecular interaction potential well ε, while the function $D_z(r_c)$ is of an extremal character: at $r_c \simeq 1.1\sigma$ the curve has a maximum [1].

It is natural and necessary to consider the question of whether under conditions where the attractive component of the gas interaction potential with the capillary wall can be neglected, Eq. (8) will transform to the well-known expression for the Knudsen diffusion coefficient [6]: $D_c = \dfrac{4}{3} \sqrt{\dfrac{2kT}{\pi m}} r_c$ Such a transformation can be expected for $kT/\varepsilon \gg 1$, $r_c/\sigma \gg 1$.

Since transverse motion of the gas molecule in the capillary is limited, the mean over time

$$\left\langle \frac{d}{dt} (\mathbf{R} \cdot \mathbf{v}_R) \right\rangle = \langle v_R^2 \rangle + \frac{1}{m} \langle (\mathbf{R} \cdot \mathbf{F}) \rangle = 0,$$

where $\mathbf{v}_R$ is the radial component of the molecular velocity. Hence the virial $\langle (\mathbf{R} \cdot \mathbf{F}) \rangle = -m \langle v_R^2 \rangle = -kT$. Under the conditions $kT/\varepsilon \gg 1$, $r_c/\sigma \gg 1$ the major contribution to the mean will be produced by terms from the repulsive component of the system potential U and it can be assumed that $|\mathbf{R}| \simeq r_c - \sigma$. Then $\langle (\mathbf{R} \cdot \mathbf{F}) \rangle = \langle |R| \cdot |F| \cos \widehat{R \cdot F} \rangle \simeq (r_c - \sigma) \langle |F| \rangle = -kT$ since R and F are collinear, i.e., we obtain $\langle |F| \rangle \simeq -kT/(r_c - \sigma)$. The quantity $\langle |F| \rangle$ can be estimated in a simpler manner: in the absence of a surface force field the change in direction of gas molecule motion v_R due to interaction with the wall is equivalent to the action of some mean force $\langle |F| \rangle$, which acts from the wall at a distance of the order of σ and is not a function of R. Therefore we may write that $U = \int_0^{r_c - \sigma} \langle |F| \rangle \, dR = -kT$, whence $\langle |F| \rangle = -kT/(r_c - \sigma)$. Assuming that $\langle F^2 \rangle \simeq \langle |F| \rangle^2$ and substituting the value of $\langle |F| \rangle$ in Eq. (8), we obtain

$$D_z \simeq \sqrt{\frac{kT}{m}} (r_c - \sigma). \tag{10}$$

Considering that for wide capillaries $r_c \gg \sigma$, we have

$$D_z \simeq \sqrt{\frac{kT}{m}} r_c \tag{11}$$

To the accuracy of a numerical factor of 1.06 this expression coincides with the Knudsen diffusion coefficient.

Thus, the asymptotic study of Eq. (8) confirms the validity of the approach used in the present study. Equation (8) encompasses the entire temperature range and a wide range of capillary radii, including the Knudsen diffusion range.

NOTATION

ρ, mean-squared displacement; t, τ, time; D, Diffusion coefficient; r, displacement; m, mass; v, velocity; k, Boltzmann constant; T, absolute temperature; r_c, capillary radius; u, intermolecular potential; ε, maximum attraction energy of molecules; σ, distance at which the molecular potential is equal to zero; U, system potential; F, force; R, distance between a molecule and capillary axis; A, autocorrelation velocity function; $F^{(1)}$, force derivatives; $\varkappa$, trajectory; K, kinetic energy.

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