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Corresponding Member of the Academy of Sciences of the USSR B. V. Deryagin and S. P. Bakanov

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Abstract

Full Text

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THEORY OF THE MOTION OF SMALL AEROSOL PARTICLES IN A DIFFUSION FIELD

§ 1. Previously ([1]-[3]) the forces acting in a diffusion field on an aerosol particle with radius r, much greater than the mean free paths of the molecules λ_1, λ_2, were considered. The starting point was a consideration of the influence of a Stefan flow with allowance for the boundary conditions at the particle surface. One of these is the absence of slip of the gas mixture at the particle surface under isothermal conditions. This condition is violated in the presence of a temperature gradient, giving rise to thermophoresis phenomena. The question arises whether there exists a slip phenomenon and a "phoresis" caused by a concentration gradient, the allowance for which is necessary to complete the theory of the behavior of aerosol particles in diffusion fields. However, a rigorous gas-kinetic calculation of such "diffusiophoresis" is complicated by the fact that the distribution of velocities of gas molecules in a layer of thickness λ depends on the distance to the particle surface. The problem is simplified for $r \ll \lambda_1, \lambda_2$, when the distribution of velocities of the molecules striking the particle surface is not disturbed by its presence.

§ 2. Consider a mixture of gases with molecular masses m_1 and $m_2 > m_1$ in the presence of small gradients of the partial concentrations n_1 and n_2, satisfying the condition $\operatorname{grad}(n_1 + n_2) = \operatorname{grad} p/kT = 0$ (p is the total pressure).

Let the velocities of two molecules of the first component of the mixture before mutual collision be $\mathbf{c}_1$ and $\mathbf{c}$, and after it $\mathbf{c}_1'$ and $\mathbf{c}'$; for the second component, respectively, $\mathbf{c}_2, \mathbf{c}$ and $\mathbf{c}_2', \mathbf{c}'$. Correspondingly we denote: $\Phi(\mathbf{c}) = \Phi$, $\Phi(\mathbf{c}') = \Phi'$, etc. In particular, if $f(\mathbf{c}, \mathbf{r})$ and $F(\mathbf{c}, \mathbf{r})$ are the velocity-distribution functions of the molecules of the first and second components, then $f(\mathbf{c}_1, \mathbf{r}) = f_1$, etc., $F(\mathbf{c}_2, \mathbf{r}) = F_2$, etc. If b_1 is the impact parameter* of molecules of the first kind among themselves, their relative velocity before impact is g_1, and the azimuth of the collision plane is ε_1, then the probability of collision is $g_1 b_1 db_1 d\varepsilon_1 = k_1 d\mathbf{k}$. For molecules of the second kind we analogously introduce $k_2 d\mathbf{k}$, and for molecules of different kinds $k_{12} d\mathbf{k}$. The kinetic equations have the form

$$\mathbf{c}_1 \frac{\partial f_1}{\partial \mathbf{r}} = \iint (f' f_1' - f f_1) k_1 \, d\mathbf{k} \, d\mathbf{c} + \iint (f_1' F_2' - f_1 F_2) k_{12} \, d\mathbf{k} \, d\mathbf{c}_2,$$
$$\mathbf{c}_2 \frac{\partial F_2}{\partial \mathbf{r}} = \iint (F' F_2' - F F_2) k_2 \, d\mathbf{k} \, d\mathbf{c} + \iint (f_1' F_2' - f_1 F_2) k_{12} \, d\mathbf{k} \, d\mathbf{c}_1. \quad (1)$$

Following (^{4}), we shall seek the solution of system (1) in the form

$$f_1 = f_1^{(0)} [1 - \mathbf{D}_1 \operatorname{grad} n_1], \qquad F_2 = F_2^{(0)} [1 - \mathbf{D}_2 \operatorname{grad} n_1], \quad (2)$$

where $f_1^{(0)}$ and $F_2^{(0)}$ are the equilibrium distribution functions of each component in a coordinate system rigidly connected with the center of mass of the mixture, $\mathbf{D}_1 = \mathbf{c}_1 D(c_1)$, $\mathbf{D}_2 = \mathbf{c}_2 D(c_2)$, where $D(c_1)$ and $D(c_2)$ are scalar functions.

* The impact parameter is the length of the perpendicular from the scattering center to the trajectory of the molecule before collision.

We shall seek the unknown functions $\mathbf{D}_1$ and $\mathbf{D}_2$ in the form of expansions

$$\mathbf{D}_1 = \sum_{-\infty}^{\infty} d_p \mathbf{a}_1^{(p)}, \qquad \mathbf{D}_2 = \sum_{-\infty}^{\infty} d_p \mathbf{a}_2^{(p)}, \quad (3)$$

where

$$\mathbf{a}_1^{(0)} = \frac{\rho_1 \rho_2}{\rho n_1 m_1^{1/2}} \mathbf{C}_1, \qquad \mathbf{a}_1^{(p)} = \mathbf{C}_1 S_{3/2}^{(p)}(C_1^2) \quad \text{for } p > 0;$$
$$\mathbf{a}_2^{(0)} = -\frac{\rho_1 \rho_2}{\rho n_2 m_2^{1/2}} \mathbf{C}_2, \qquad \mathbf{a}_2^{(p)} = \mathbf{C}_2 S_{3/2}^{(p)}(C_2^2) \quad \text{for } p < 0; \quad (4)$$

ρ_1 and ρ_2 are the densities of the first and second components; $\rho = \rho_1 + \rho_2$; $S_{3/2}^{(p)}(C_1^2)$ are Sonine polynomials; $\mathbf{C}_1 = (m_1/2kT)^{1/2} \mathbf{c}_1$; $\mathbf{C}_2 = (m_2/2kT)^{1/2} \mathbf{c}_2$.

If, in equation (1), instead of f_1 and F_2 we substitute their values (2) and take into account that

$$\frac{\partial f_1^{(0)}}{\partial \mathbf{r}} = \frac{f_1^{(0)}}{n_1} \operatorname{grad} n_1, \qquad \frac{\partial F_2^{(0)\prime}}{\partial \mathbf{r}} = -\frac{F_2^{(0)}}{n_2} \operatorname{grad} n_1, \qquad f^{(0)} f_1^{(0)} = f^{(0)\prime} f_1^{(0)\prime},$$

$$f_1^{(0)} F^{(0)} = f_1^{(0)\prime} F_2^{(0)\prime}, \qquad F^{(0)} F_2^{(0)} = F^{(0)\prime} F_2^{(0)\prime},$$

then, after cancellation by $\operatorname{grad} n_1$, we obtain:

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$$-\mathbf{c}_1 \frac{f_1^{(0)}}{n_1} = \iint f^{(0)} f_1^{(0)} (\mathbf{D}_1' + \mathbf{D}' - \mathbf{D}_1 - \mathbf{D})\, k_1 \, d\mathbf{k}\, d\mathbf{c} +$$

$$+ \iint f_1^{(0)} F_2^{(0)} (\mathbf{D}_1' + \mathbf{D}_2' - \mathbf{D}_1 - \mathbf{D}_2)\, k_{12}\, d\mathbf{k}\, d\mathbf{c}_2, \tag{5}$$

$$\mathbf{c}_2 \frac{F_2^{(0)}}{n_2} = \iint F^{(0)} F_2^{(0)} (\mathbf{D}' + \mathbf{D}_2' - \mathbf{D} - \mathbf{D}_2)\, k_2\, d\mathbf{k}\, d\mathbf{c} +$$

$$+ \iint f_1^{(0)} F_2^{(0)} (\mathbf{D}_1' + \mathbf{D}_2' - \mathbf{D}_1 - \mathbf{D}_2)\, k_{12}\, d\mathbf{k}\, d\mathbf{c}_1.$$

Multiply scalarly the first and second equations (5), respectively, by $\mathbf{a}_1^{(p)}\, d\mathbf{c}_1$ and $\mathbf{a}_2^{(p)}\, d\mathbf{c}_2$, integrate over all possible $\mathbf{c}_1$ and $\mathbf{c}_2$, and add:

$$\frac{1}{n_2} \int F_2^{(0)} \mathbf{c}_2 \cdot \mathbf{a}_2^{(p)}\, d\mathbf{c}_2 - \frac{1}{n_1} \int f_1^{(0)} \mathbf{c}_1 \cdot \mathbf{a}_1^{(p)}\, d\mathbf{c}_1 =$$

$$= \iiint f^{(0)} f_1^{(0)} (\mathbf{D}' + \mathbf{D}_1' - \mathbf{D} - \mathbf{D}_1) \mathbf{a}_1^{(p)} k_1\, d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{c} +$$

$$+ \iiint f_1^{(0)} F_2^{(0)} (\mathbf{D}_1' + \mathbf{D}_2' - \mathbf{D}_1 - \mathbf{D}_2)(\mathbf{a}_1^{(p)} + \mathbf{a}_2^{(p)}) k_{12}\, d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{c}_2 +$$

$$+ \iiint F^{(0)} F_2^{(0)} (\mathbf{D}' + \mathbf{D}_2' - \mathbf{D} - \mathbf{D}_2) \mathbf{a}_2^{(p)} k_2\, d\mathbf{k}\, d\mathbf{c}\, d\mathbf{c}_2. \tag{6}$$

Denote the expression obtained by $n_1 n_2 \delta_p$. From the orthogonality condition for the Sonine polynomials it follows that

$$\delta_p = 3(2kT)^{1/2}/2n_1 n_2 \quad \text{for } p = 0; \qquad \delta_p = 0 \quad \text{for } p \neq 0. \tag{7}$$

If, in equality (6), instead of $\mathbf{D}_1$ and $\mathbf{D}_2$ we substitute expressions (3), then it decomposes into the system of equations

$$\delta_p = \sum_{-\infty}^{\infty} d_q a_{pq}, \tag{8}$$

in which d_q are unknowns, and a_{pq} is an expression of the form

$$a_{pq} = \frac{1}{n_1 n_2} \Big\{ \iiint f^{(0)} f_1^{(0)} (\mathbf{a}^{(q)\prime} + \mathbf{a}_1^{(q)\prime} - \mathbf{a}^{(q)} - \mathbf{a}_1^{(q)}) \mathbf{a}_1^{(p)} k_1\, d\mathbf{k}\, d\mathbf{c}\, d\mathbf{c}_1 +$$

$$+\iiint f_1^{(0)}F_2^{(0)}(\mathbf{a}_1^{(q)\prime}+\mathbf{a}_2^{(q)\prime}-\mathbf{a}_1^{(q)}-\mathbf{a}_2^{(q)})(\mathbf{a}_1^{(p)}+\mathbf{a}_2^{(p)})k_{12}\,d\mathbf{c}\,d\mathbf{c}_1\,d\mathbf{c}_2+$$

$$+\iiint F^{(0)}F_2^{(0)}(\mathbf{a}^{(q)\prime}+\mathbf{a}_2^{(q)\prime}-\mathbf{a}^{(q)}-\mathbf{a}_2^{(q)})\mathbf{a}_2^{(p)}k_2\,d\mathbf{k}\,d\mathbf{c}\,d\mathbf{c}_2\Big\}. \qquad (9)$$

The system (8) is solved by the method of successive approximations. Let us consider the zeroth approximation, setting $q=0$. The system degenerates into a single equation $\delta_0=d_0a_{00}$. Hence

$$\mathbf{D}_1^{(0)}=\frac{\delta_0 a_1^{(0)}}{a_{00}}, \qquad \mathbf{D}_2^{(0)}=\frac{\delta_0 a_2^{(0)}}{a_{00}}.$$

In the first approximation ($q=-1,0,1$)

$$\begin{aligned} d_{-1}a_{-1-1}+d_0a_{0-1}+d_1a_{1-1}&=0,\\ d_{-1}a_{-10}+d_0a_{00}+d_1a_{10}&=\delta_0,\\ d_{-1}a_{-11}+d_0a_{01}+d_1a_{11}&=0. \end{aligned} \qquad (10)$$

Denoting the determinant of the system (10) by A, we obtain

$$d_{-1}=-\frac{\delta_0}{A}\begin{vmatrix} a_{0-1} & a_{1-1}\\ a_{01} & a_{11}\end{vmatrix}, \quad d_0=\frac{\delta_0}{A}\begin{vmatrix} a_{-1-1} & a_{1-1}\\ a_{1-1} & a_{11}\end{vmatrix}, \quad d_1=-\frac{\delta_0}{A}\begin{vmatrix} a_{-1-1} & a_{0-1}\\ a_{-11} & a_{01}\end{vmatrix}, \qquad (11)$$

$$\mathbf{D}_1^{(1)}=d_0a_1^{(0)}+d_1a_1^{(1)}, \qquad \mathbf{D}_2^{(1)}=d_0a_2^{(0)}+d_{-1}a_2^{(1)}. \qquad (12)$$

Thus the problem of finding the distribution functions in any approximation reduces to the calculation of the corresponding integrals a_{pq} (see (4)).

The relations (11) take the form

$$d_{-1}=-\frac{3}{2n_1n_2}\left(\frac{m_0M_1M_2}{\pi}\right)^{1/2}\frac{B'_{-1}}{A'm_0^{1/2}\sigma_{12}^2}, \qquad d_0=\frac{3}{2n_1n_2}\left(\frac{m_0M_1M_2}{\pi}\right)^{1/2}\frac{B'_0}{A'm_0\sigma_{12}^2},$$

$$d_1=-\frac{3}{2n_1n_2}\left(\frac{m_0M_1M_2}{\pi}\right)^{1/2}\frac{B'_1}{A'm_0^{1/2}\sigma_{12}^2}, \qquad (13)$$

where B'_0, B'_1, B'_{-1}, and A' are dimensionless quantities corresponding to the determinants (11); $m_0=m_1+m_2$; $M_1=m_1/m_0$; $M_2=m_2/m_0$; σ_1 and σ_2

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are the diameters of the molecules of the first and second components; $\sigma_{12} = (\sigma_1 + \sigma_2)/2$.

The distribution functions found describe, in the first approximation, the field of mutual diffusion of two gases

$$f_1^{(1)} = n_1 \left(\frac{m_1}{2\pi kT}\right)^{3/2} e^{-C_1^2} \left\{1 + \left[d_0 \frac{\rho_1\rho_2}{\rho n_1 m_1^{1/2}} + d_1 S_{1/2}^{(1)}(C_1^2)\right] C_1 \operatorname{grad} n_1 \cos\vartheta_1\right\}, \tag{14}$$

$$F_2^{(1)} = n_2 \left(\frac{m_2}{2\pi kT}\right)^{3/2} e^{-C_2^2} \left\{1 + \left[-d_0 \frac{\rho_1\rho_2}{\rho n_2 m_2^{1/2}} + d_{-1} S_{1/2}^{(1)}(C_2^2)\right] C_2 \operatorname{grad} n_2 \cos\vartheta_2\right\}, \tag{15}$$

where ϑ_1 and ϑ_2 are the angles made by C_1 and C_2 with the direction opposite to $\operatorname{grad} n_1$.

§ 3. An aerosol particle in a diffusion field, in addition to Brownian motion, possesses an ordered velocity $\mathbf{u}$ for which the mean momentum transferred to the particle in molecular collisions is equal to zero. We shall consider such small values of $\operatorname{grad} n_1$ for which $\mathbf{u} \sim \operatorname{grad} n_1 \ll c_2$. In what follows we shall neglect terms proportional to u^2 and $\mathbf{u} \cdot \operatorname{grad} n_1$.

The momentum dp_1, transferred in collisions by molecules of the first component per unit time to the element dS of the surface of the spherical particle in the direction $\mathbf{u}$, is equal to

$$dp_1 = \int m_1 (c_1 + u)_u (c_1 + u)_n f_1 \, dc_1 \, dS, \tag{16}$$

where $(c_1+u)_u$ and $(c_1+u)_n$ are the projections of the vector c_1+u, respectively, on the directions $\mathbf{u}$ and of the normal $\mathbf{n}$ to dS. If the angles between c_1 and $\mathbf{n}$ are denoted by ψ_1, between $\mathbf{u}$ and $\mathbf{n}$ by θ, and the azimuth of c_1 in the system connected with $\mathbf{n}$ by φ, then $\cos\vartheta_1 = \cos\psi_1 \cos\theta + \sin\psi_1 \sin\theta \cos\varphi$. Expanding the equality (16):

$$dp_1 = m_1 \int (c_1 \cos\vartheta_1 + u)(c_1 \cos\psi_1 + u\cos\theta)\, n_1 \left(\frac{m_1}{2\pi kT}\right)^{3/2} e^{-C_1^2} \times$$

$$\times \left\{1 + \left[d_0 \frac{\rho_1\rho_2}{\rho n_1 m_1^{1/2}} + d_1 S_{1/2}^{(1)}(C_1^2)\right] C_1 \operatorname{grad} n_1 \cos\vartheta_1\right\} c_1^2 dc_1 \sin\psi_1 d\psi_1 d\varphi.$$

Integration with allowance for the above conditions gives

$$p_1 = -m_1 n_1 \bar{c}_1 \frac{\cos^2\theta + 1}{2} \left\{ \left(\frac{kT}{8m_1} \right)^{1/2} \left[d_0 \frac{\rho_1 \rho_2}{\rho n_1 m_1^{1/2}} - \frac{1}{2} d_1 \right] \operatorname{grad} n_1 + \frac{u}{2} \right\}. \tag{17}$$

Similarly, for the momentum transmitted by molecules of the second component, we have

$$p_2 = -m_2 n_2 \bar{c}_2 \frac{\cos^2\theta + 1}{2} \left\{ \left(\frac{kT}{8m_2} \right)^{1/2} \left[-d_0 \frac{\rho_1 \rho_2}{\rho n_2 m_2^{1/2}} - \frac{1}{2} d_{-1} \right] \operatorname{grad} n_1 + \frac{u}{2} \right\}. \tag{18}$$

As for the recoil momentum in the evaporation of molecules from the surface of the particle, in the case of specular reflection it is equal to zero. For another law of reflection it is easy to calculate the additional momentum, which, however, does not change the order of magnitude of u. Equating the sum $p_1 + p_2$ to zero, we find:

$$u = \left(\frac{kT}{8} \right)^{1/2} \frac{\operatorname{grad} n_1}{n_1 m_1^{1/2} + n_2 m_2^{1/2}} \left[2d_0 \frac{\rho_1 \rho_2}{\rho} \left(\frac{1}{m_2^{1/2}} - \frac{1}{m_1^{1/2}} \right) + n_1 d_1 + n_2 d_{-1} \right]. \tag{19}$$

To pass to the reference frame connected with the walls of the vessel containing the diffusing mixture, we take into account that the total flux of the number of molecules through an area rigidly connected with the walls is equal to zero. From this condition one immediately obtains, in the indicated system, the velocity of the center of mass of the mixture, which, together with (19), gives the velocity u' relative to the walls:

$$u' = -\frac{3}{2} \left(\frac{m_0 M_1 M_2 kT}{2\pi} \right)^{1/2} \frac{\operatorname{grad} n_1}{A' \sigma_{12}^2 \rho_2} \left\{ \frac{B_0' M_2}{1 + n_{12} m_{12}} \left[\frac{1 - \sqrt{m_{12}}}{1 + n_{21}\sqrt{m_{21}}} - \frac{m_{12} - 1}{1 + n_{21}} \right] + \frac{(B_1' + n_{21} B_{-1}') M_2^{1/2}}{2(n_{21} + \sqrt{m_{12}})} \right\}, \tag{20}$$

where $m_{12} = m_1/m_2,\ m_{21} = m_2/m_1,\ n_{12} = n_1/n_2,\ n_{21} = n_2/n_1$.

A numerical calculation for the case of an air-water vapor mixture ($p = 1$ atm., $T = 293^\circ$ K) gives $u' = 1.47 \cdot 10^{-2}/l$ (cm/sec), where l is the distance, in centimeters, over which the relative humidity falls from 100% to zero.

Let us note that the first term in the curly brackets of equality (20) is connected with the diffusion coefficient of the mixture*.

In conclusion we point out that, for a highly porous body in which a pseudo-molecular flow regime can occur, the following phenomenon should take place.

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Let a porous partition separate two vessels with different concentrations of a gas mixture. The quasi-stationary state in such a system will correspond to the presence of a difference in total pressure. This pressure difference must cause a flow of the gas mixture with the linear velocity u', compensating its motion through the pores of the partition. The indicated pressure difference must be directly proportional to the concentration difference on the two sides of the porous partition and inversely proportional to the mean cross section of the pores, and can be measured with a manometer, as was discovered still earlier by G. A. Batova.

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* We express our gratitude to O. M. Todes, who drew our attention to this circumstance.

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

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