

## DIFFUSIOPHORESIS OF AN AEROSOL PARTICLE IN A BINARY GAS MIXTURE

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*The diffusion force and rate are calculated for the diffusiophoresis of a spherical particle in a binary gas mixture by solving the gas-kinetic equations. Two schemes of diffusiophoresis are considered: constant-pressure diffusion and diffusion of one mixture component through the other fixed component. The problem is solved by the integral-momentum method at arbitrary Knudsen numbers. Diffuse scattering of the gas molecules on the particle surface is assumed. The Lorentzian and Rayleigh models of a binary gas mixture are considered. The dependences of the force and rate of diffusiophoresis on the Knudsen number and the other determining parameters are analyzed. The results obtained are compared with well-known experimental data.*

**Introduction.** Diffusiophoresis is the process in which a particle placed in a gas mixture of nonuniform concentration is acted upon by a force which sets this particle in motion. For the free-molecular flow regime, diffusiophoresis has been studied theoretically by direct calculation of the momentum transferred to the particle by the gas molecules [1–4], and for the viscous regime, it has been studied by solving the Stokes equations with the boundary condition of diffusion slip [5, 6] and by invoking methods of the thermodynamics of irreversible processes [7, 8].

Brock [9] performed a study, primarily of a methodological character, in which the diffusiophoresis force and rate were calculated for the first time at intermediate Knudsen numbers  $\text{Kn} = l/R_0$  ( $l$  is the mean free path of the molecules and  $R_0$  is the particle radius).

Annis et al. [10] used the method of “giant molecules,” in which aerosol particles are treated as a gas-mixture component. The expression obtained by this method for the diffusiophoresis rate includes a number of adjustable parameters that follow from comparison of theory with experiment. The accuracy of this method is not known *a priori*. The results obtained in [10] require theoretical verification based on solving the gas-kinetic equation at arbitrary Knudsen numbers. It should be noted that until now there has not been adequate theory for diffusiophoresis. Scanty experimental data [4, 11, 12] that can be used for a quantitative comparison with theoretical results have been obtained primarily for intermediate Knudsen numbers.

The purpose of the present work is to develop a molecular-kinetic model for the diffusiophoresis of aerosols in binary gas mixtures for arbitrary  $\text{Kn}$ .

**1. Formulation of the Problem.** We consider a spherical particle of radius  $R_0$  suspended in a binary gas mixture with a uniform temperature a fixed concentration gradient  $|\nabla x_1|_\infty = -|\nabla x_2|_\infty$  directed along the  $OZ$  axis collinearly to the hydrodynamic (mass-average) velocity  $\mathbf{V}_\infty$  of the incoming flow (Fig. 1). We introduce the following notation:  $x_\alpha = n_\alpha/n$  is the concentration of the species  $\alpha$  ( $\alpha = 1$  for species 1 and 2 for species 2) and  $n = n_1 + n_2$  is the number density of the gas mixture.

The partial number densities of the components away from the particle are given by

$$n_{\alpha\infty} = n_\alpha \Big|_{r \rightarrow \infty} = n_{\alpha 0} \left( 1 + \left| \nabla x_\alpha \right|_\infty z/x_\alpha \right), \quad n_{\alpha 0} = n_{\alpha\infty} \Big|_{\theta = \pm \pi/2}.$$

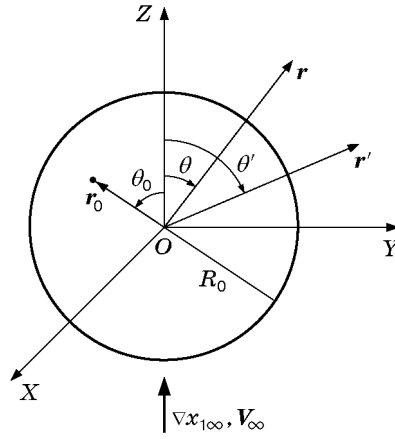


Fig. 1. Geometry of the problem.

If the Mach number is small, the velocity distribution functions of the molecules can be written in linearized form

$$f_\alpha = f_{\alpha 0} \left( 1 + \left| \nabla x_\alpha \right|_\infty z/x_\alpha + 2c_{\alpha z} V_{\alpha\infty} + \Phi_\alpha \right), \quad (1.1)$$

where  $f_{\alpha 0} = n_{\alpha 0} (m_\alpha / (2\pi kT))^{3/2} \exp(-c_\alpha^2)$ ,  $c_\alpha = (m_\alpha / (2kT))^{1/2} \mathbf{v}_\alpha$ ,  $V_{\alpha\infty} = (m_\alpha / (2kT))^{1/2} V_\infty \ll 1$  is the nondimensional mass-average velocity of the mixture (Mach number with accuracy up to a constant factor),  $\Phi_\alpha$  is the unknown perturbation of the distribution function for molecules of the species  $\alpha$ ,  $\mathbf{v}_\alpha$  and  $m_\alpha$  are the velocity and mass of molecules of the species  $\alpha$ ,  $T$  is the temperature of the mixture, and  $k$  is the Boltzmann constant.

To find the function  $\Phi_\alpha$ , we use the linearized Boltzmann equation (see, e.g., [13])

$$\mathbf{v}_\alpha \cdot \nabla \Phi_\alpha + \frac{v_{\alpha z} \left| \nabla x_\alpha \right|_\infty}{x_\alpha} = \sum_\beta L_{\alpha\beta}(\Phi_\alpha). \quad (1.2)$$

For the further calculations, we employ the approximating collision integral of the second approximation [14], which has the form

$$\begin{aligned} L_{\alpha\beta}^{(2)}(\Phi_\alpha) = & -\gamma_{\alpha\beta} \Phi_\alpha + \gamma_{\alpha\beta} \nu_\alpha + 2c_{\alpha i} \left[ \gamma_{\alpha\beta} u'_{\alpha i} - \left( u'_{\alpha i} - \sqrt{m_\alpha/m_\beta} u'_{\beta i} \right) \nu_{\alpha\beta}^{(1)} \right] \\ & + 2c_{\alpha i} c_{\alpha j} \left[ (\gamma_{\alpha\beta} - \nu_{\alpha\beta}^{(3)}) \pi_{\alpha ij} + \nu_{\alpha\beta}^{(4)} \pi_{\beta ij} \right]. \end{aligned} \quad (1.3)$$

Here

$$\begin{aligned} \nu_\alpha = \frac{n_\alpha - n_{\alpha\infty}}{n_{\alpha 0}} = \pi^{-3/2} \int \exp(-c_\alpha^2) \Phi_\alpha dc_\alpha, \quad u'_{\alpha i} = u_{\alpha i} - V_{\alpha\infty} \delta_{iz} = \pi^{-3/2} \int \exp(-c_\alpha^2) c_{\alpha i} \Phi_\alpha dc_\alpha, \\ \pi_{\alpha ij} = \frac{P_{\alpha ij}}{2p_{\alpha 0}} = \pi^{-3/2} \int \exp(-c_\alpha^2) \left( c_{\alpha i} c_{\alpha j} - \frac{\delta_{ij} c_\alpha^2}{3} \right) \Phi_\alpha dc_\alpha, \end{aligned}$$

$\gamma_{\alpha\beta}$  are the effective frequencies of collision between molecules of the species  $\alpha$  and  $\beta$ ,  $\nu_\alpha$  is the relative perturbation of the number density of molecules of the species  $\alpha$  near the aerosol particle,  $u'_{\alpha i}$  is the nondimensional velocity of the species  $\alpha$  relative to the hydrodynamic velocity of the incoming flow, which has the meaning of the nondimensional rate of diffusion of the species  $\alpha$  away from the particle,  $\pi_{\alpha ij}$  is the dimensional nondivergent stress tensor for the species  $\alpha$ ,  $p_{\alpha 0} = n_{\alpha 0} kT$  is the equilibrium partial pressure, and  $\delta_{iz}$  is the Kronecker delta. The expressions for the frequencies  $\nu_{\alpha\beta}^{(1)}$ ,  $\nu_{\alpha\beta}^{(3)}$ , and  $\nu_{\alpha\beta}^{(4)}$  are given in [14].

In the extreme case of small Knudsen numbers, the model collision integral (1.3) describes diffusion and internal friction in a gas mixture in exact accordance with the first approximation of the Chapman–Enskog theory [13], which should ensure an adequate description of diffusiophoresis. Expression (1.3) takes into account that gas temperature is uniform over the entire region up to the particle surface and the temperatures of the mixture components are identical. Hence, we can restrict ourselves to the second approximation of the model collision operator [14]. Of course, the one-temperature approximation is valid only within the framework of linear theory

(see, e.g., [15]). At the same time, although the temperatures of the components are identical away from the particle, they may be different near the particle provided that the thermal polarizations of the components are different. However, the thermal polarization of the gas and the particle, which is due to isothermal heat transfer in the gas and the finite thermal conductivity of the particle, makes an insignificant contribution (about 0.2%) to the momentum transfer [16] and, therefore, is not considered in the present paper.

At large distances from the particle, its effect on the state of the gas weakens. For  $r \rightarrow \infty$ , the perturbation function  $\Phi_{\alpha\infty} = \Phi_{\alpha}|_{r \rightarrow \infty}$  is spatially homogeneous, i.e.,  $\nabla\Phi_{\alpha\infty} = 0$ . Therefore, the solution of Eq. (1.2) without the first term on the left side and with the collision integral (1.3) has the form

$$\Phi_{\alpha\infty} = 2c_{\alpha z}u'_{\alpha\infty}, \quad u'_{\alpha\infty} = -\frac{1}{2\nu_{\alpha\beta}^{(1)}}\frac{\rho_{\beta}}{\rho}\left(\frac{2kT}{m_{\alpha}}\right)^{1/2}\frac{|\nabla x_{\alpha}|_{\infty}}{x_{\alpha}}, \quad \rho_{\alpha} = n_{\alpha}m_{\alpha}, \quad \rho = \rho_1 + \rho_2.$$

In addition, away from the particle, Eqs. (1.2) and (1.3) lead to the following relationship between the diffusion rates:

$$\nu_{\alpha\beta}^{(1)}\left[u'_{\alpha\infty} - \left(\frac{m_{\alpha}}{m_{\beta}}\right)^{1/2}u'_{\beta\infty}\right] = -\frac{1}{2}\left(\frac{2kT}{m_{\alpha}}\right)^{1/2}\frac{|\nabla x_{\alpha}|_{\infty}}{x_{\alpha}}. \quad (1.4)$$

We note that expression (1.4) coincides with the result of the first Chapman–Enskog approximation [13].

We introduce the notation  $\Phi_{\alpha} = \Phi_{\alpha\infty} + h_{\alpha}$ , where  $h_{\alpha}$  is the perturbation of the distribution function for molecules of the species  $\alpha$  due to the presence of the particle. In this case, the partial velocities are written as

$$u'_{\alpha i} = u'_{\alpha\infty}\delta_{iz} + w_{\alpha i}, \quad w_{\alpha i} = \pi^{-3/2}\int c_{\alpha i}\exp(-c_{\alpha}^2)h_{\alpha}dc_{\alpha},$$

where  $w_{\alpha i}$  is the perturbation of the nondimensional velocity  $u'_{\alpha i}$  near the particle.

The functions  $h_{\alpha}$  satisfy the following system of kinetic equations:

$$\mathbf{v}_{\alpha} \cdot \nabla h_{\alpha} = \sum_{\beta=1}^2 L_{\alpha\beta}^{(2)}(h_{\alpha}) \quad (\alpha = 1, 2). \quad (1.5)$$

The form of  $L_{\alpha\beta}^{(2)}(h_{\alpha})$  follows from expression (1.3) after replacement of  $u'_{\alpha i}$  by  $w_{\alpha i}$ .

As the boundary conditions, we assume that the molecules of both components are diffusely scattered on the particle surface with the Maxwell velocity distribution

$$f_{\alpha}^{+} = f_{\alpha 0}[1 + A_{\alpha}(\theta_0)], \quad (1.6)$$

where  $A_{\alpha}$  are reflection parameters that describe the number densities of the scattered molecules and depend on the polar angle  $\theta_0$  (Fig. 1).

With allowance for expressions (1.1) and (1.6), the boundary conditions for the perturbation functions have the form

$$h_{\alpha}^{+} = A_{\alpha}(\theta_0) - \left(\frac{|\nabla x_{\alpha}|_{\infty}}{x_{\alpha}}\right)R_0 \cos\theta_0 - 2c_{\alpha z}V_{\alpha\infty} - 2c_{\alpha z}u'_{\alpha\infty}, \quad c_{\alpha r} > 0. \quad (1.7)$$

The boundary-value problem (1.5)–(1.7) is linear and includes two independent generalized forces  $\left|\nabla x_1\right|_{\infty}R_0$  and  $V_{1\infty}$ . Therefore, we can write

$$h_{\alpha} = h_{\alpha}^D\left|\nabla x_1\right|_{\infty}R_0 + h_{\alpha}^F V_{1\infty}, \quad A_{\alpha} = A_{\alpha}^D\left|\nabla x_1\right|_{\infty}R_0 + A_{\alpha}^F V_{1\infty}. \quad (1.8)$$

The macroscopic quantities are represented similarly:

$$\nu_{\alpha} = \nu_{\alpha}^D\left|\nabla x_1\right|_{\infty}R_0 + \nu_{\alpha}^F V_{1\infty}, \quad w_{\alpha i} = w_{\alpha i}^D\left|\nabla x_1\right|_{\infty}R_0 + w_{\alpha i}^F V_{1\infty}, \quad (1.9)$$

$$\pi_{\alpha ij} = \pi_{\alpha ij}^D\left|\nabla x_1\right|_{\infty}R_0 + \pi_{\alpha ij}^F V_{1\infty}.$$

Substituting (1.8) and (1.9) into Eqs. (1.5) and (1.7) and selecting terms proportional to  $\left|\nabla x_1\right|_{\infty}R_0$  and  $V_{1\infty}$ , we obtain

$$\mathbf{v}_\alpha \cdot \nabla h_\alpha^{D,F} = \sum_\beta L_{\alpha\beta}^{(2)}(h_\alpha^{D,F}); \quad (1.10)$$

$$h_\alpha^{D+} = A_\alpha^D + \frac{(-1)^\alpha}{x_\alpha} \left[ \cos \theta_0 - \frac{c_{\alpha z}}{\nu_{\alpha\beta}^{(1)}} \frac{\rho_\beta}{\rho} \frac{1}{R_0} \left( \frac{2kT}{m_\alpha} \right)^{1/2} \right]; \quad (1.11)$$

$$h_\alpha^{F+} = A_\alpha^F - 2c_{\alpha z} (m_\alpha/m_1)^{1/2}. \quad (1.12)$$

The reflection parameters  $A_\alpha^D$  and  $A_\alpha^F$  are obtained from the nonpenetration conditions, which imply the equality of number flows for reflected and incoming molecules on the particle surface:

$$\left| N_\alpha^{D,F+} \right|_{r=R_0} = \left| N_\alpha^{D,F-} \right|_{r=R_0}. \quad (1.13)$$

Thus, the complete problem is split into two problems:

- 1) the problem of the diffusion force acting on the particle which is at rest relative to the center of mass of the gas mixture [Eq. (1.10) with the superscript  $D$  and Eq. (1.11)];
- 2) the problem of the drag force of the particle in a homogeneous flow of the gas mixture [Eq. (1.10) with the superscript  $F$  and Eq. (1.12)].

We assume that the concentration of one of the mixture components is small  $n_1 \ll n_2$ . It can be shown that neglect of the first-order terms  $O(n_1/n_2)$  reduces problem 2 to the problem of the drag force in a single-component gas (second component of the mixture), whose solution is known (see, e.g., [16]). Thus, it remains to calculate the diffusion force.

The next simplification is related to the assumption on the ratio of molecular weights of the mixture components. Let us consider two models:

- 1) a Lorentzian mixture, in which  $m_1/m_2 \ll 1$ ;
- 2) a Rayleigh mixture in which  $m_1/m_2 \gg 1$ .

We write the effective collision frequencies in the integral  $L_{\alpha\beta}^{(2)}$  in the forms  $\gamma_{12} = \nu_{12}^{(3)}$  and  $\gamma_{22} = \nu_{22}^{(3)} - \nu_{22}^{(4)}$ . This allows us to eliminate terms containing the stress tensor from expression (1.3) and thus simplify the calculations. We note that writing the effective frequencies in different form, we obtain somewhat different results for the desired macroparameters at intermediate Knudsen numbers. However, from the method of constructing approximating collision integrals [14] it follows that the difference is not large. Margilevskii and Chernyak [17] showed this by solving the problem of vaporization of a drop. Thus, depending on the form of the effective collision frequencies there may be small quantitative differences (several percent) in the calculated values of the diffusion force.

With allowance for the aforesaid, Eqs. (1.10) become

$$\mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} h_1 = -h_1 + \nu_1 + 2(1 - \varphi_{12}^{(1)})(c_{1r}w_{1r} + c_{1\theta}w_{1\theta}); \quad (1.14)$$

$$\mathbf{c}_2 \cdot \frac{\partial}{\partial \mathbf{r}_2} h_2 = -h_2 + \nu_2 + 2(c_{2r}w_{2r} + c_{2\theta}w_{2\theta}), \quad (1.15)$$

where  $\mathbf{c}_1$  and  $\mathbf{c}_2$  are the nondimensional velocities of molecules of species 1 and 2,  $\varphi_{12}^{(1)} = \nu_{12}^{(1)}/\gamma_{12}$ ,  $\mathbf{r}_1 = r\gamma_{12}(m_1/(2kT))^{1/2}$ , and  $\mathbf{r}_2 = r\gamma_{22}(m_2/(2kT))^{1/2}$ . For brevity, the superscript  $D$  is omit below.

We note that Eqs. (1.14) and (1.15) differ for the two models of the gas mixture in values of the frequencies  $\gamma_{12}$ ,  $\gamma_{22}$ , and  $\nu_{12}^{(1)}$ .

The diffusion force is determined by the total momentum transferred to the particle by molecules of the gas mixture upon collisions:

$$\begin{aligned} \mathbf{F}_D = \mathbf{n}_z \int dS \sum_\alpha \sum_\pm \int m_\alpha v_{\alpha z} v_{\alpha r} f_\alpha^\pm \Big|_{r=R_0} d\mathbf{v}_\alpha = \mathbf{n}_z \int dS \sum_\alpha m_\alpha \left[ \int_{v_r > 0} v_{\alpha z} v_{\alpha r} f_{\alpha 0} \left( 1 + A_\alpha \left| \nabla x_1 \right|_\infty R_0 \right) d\mathbf{v}_\alpha \right. \\ \left. + \int_{v_r < 0} v_{\alpha z} v_{\alpha r} f_{\alpha 0} \left( 1 + 2c_{\alpha z} u'_{\alpha\infty} + \frac{\left| \nabla x_\alpha \right|_\infty}{x_\alpha} R_0 \cos \theta_0 + h_\alpha \left| \nabla x_1 \right|_\infty R_0 \right) d\mathbf{v}_\alpha \right]. \end{aligned} \quad (1.16)$$

Here  $\mathbf{n}_z$  is a unit vector along the  $OZ$  axis,  $S$  is the particle surface area, and  $f_\alpha^-$  is the distribution function for molecules of species  $\alpha$  that are incoming on the particle surface.

The stationary rate of diffusiophoresis  $\mathbf{U}_D$  is determined from the balance of the forces acting on the particle:  $\mathbf{F}_D + \mathbf{F}_F = 0$  ( $\mathbf{F}_D$  is the diffusion force and  $\mathbf{F}_F$  is the viscous drag force of the medium).

**2. Method of Solution.** The kinetic equations (1.14) and (1.15) were integrated along the characteristics [18] with allowance for boundary conditions (1.11) and were reduced to the following system of integral equations for the macroparameters of the mixture:

$$\begin{aligned}\nu_\alpha &= \pi^{-3/2} \int_{\omega_0} X_{23}^{\alpha 0} d\omega + \pi^{-3/2} \int_{V'} \frac{X_{12}^\alpha}{|\mathbf{r}_\alpha - \mathbf{r}'_\alpha|^2} d\mathbf{r}'_\alpha, \\ w_{\alpha r} &= \pi^{-3/2} \int_{\omega_0} X_{34}^{\alpha 0} \Omega_{0r} d\omega + \pi^{-3/2} \int_{V'} \frac{X_{23}^\alpha \Omega_r}{|\mathbf{r}_\alpha - \mathbf{r}'_\alpha|^2} d\mathbf{r}'_\alpha, \\ w_{\alpha\theta} &= \pi^{-3/2} \int_{\omega_0} X_{34}^{\alpha 0} \Omega_{0\theta} d\omega + \pi^{-3/2} \int_{V'} \frac{X_{23}^\alpha \Omega_\theta}{|\mathbf{r}_\alpha - \mathbf{r}'_\alpha|^2} d\mathbf{r}'_\alpha.\end{aligned}\quad (2.1)$$

Here integration is performed along the solid angle  $\omega_0$  at which the sphere can be seen from a point with radius vector  $\mathbf{r}$  and over the space  $V'$  whose points are connected to the radius vector  $\mathbf{r}$  without intersection of the sphere. The quantities  $X_{kl}^{\alpha 0}$  and  $X_{kl}^\alpha$  are defined as follows:

$$\begin{aligned}X_{kl}^{10} &= A_1(\theta_0) I_k(|\mathbf{r}_1 - \mathbf{r}_{01}|) - \frac{1}{x_1} \left[ I_k(|\mathbf{r}_1 - \mathbf{r}_{01}|) \cos \theta_0 - \frac{\Omega_{0z}}{\nu_{12}^{(1)} R_0} \left( \frac{2kT}{m_1} \right)^{1/2} I_l(|\mathbf{r}_1 - \mathbf{r}_{01}|) \right], \\ X_{kl}^{20} &= A_2(\theta_0) I_k(|\mathbf{r}_2 - \mathbf{r}_{02}|) + \left[ I_k(|\mathbf{r}_2 - \mathbf{r}_{02}|) \cos \theta_0 - \frac{\Omega_{0z}}{\nu_{21}^{(1)} R_0} \frac{\rho_1}{\rho} \left( \frac{2kT}{m_2} \right)^{1/2} I_l(|\mathbf{r}_2 - \mathbf{r}_{02}|) \right], \\ X_{kl}^1 &= \nu_1 I_k(|\mathbf{r}_1 - \mathbf{r}'_1|) + 2(1 - \varphi_{12}^{(1)}) (w_{1r} \Omega_{r'} + w_{1\theta} \Omega_{\theta'}) I_l(|\mathbf{r}_1 - \mathbf{r}'_1|), \\ X_{kl}^2 &= \nu_2 I_k(|\mathbf{r}_2 - \mathbf{r}'_2|) + 2(w_{2r} \Omega_{r'} + w_{2\theta} \Omega_{\theta'}) I_l(|\mathbf{r}_2 - \mathbf{r}'_2|).\end{aligned}$$

Here  $I_n(z) = \int_0^\infty c^n \exp(-c^2 - z/c) dc$  and the directing-vector components  $\boldsymbol{\Omega} = (\mathbf{r} - \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$  are determined in [16].

System (2.1) is closed by the following integral nonpenetration conditions on the particle surface for each of the mixture components, which follow from Eqs. (1.13):

$$\begin{aligned}& \frac{1}{2} \int_S \left( \frac{A_1(\theta_0)}{\pi^{1/2}} - \frac{1}{2} \frac{H_1}{\varphi_{12}^{(1)}} \cos \theta_0 \right) ds \\ &= \pi^{-3/2} \int_{V_0} d\mathbf{r}_1 \int_{\omega_0} d\omega [\nu_1 I_2(|\mathbf{r}_1 - \mathbf{r}_{01}|) - 2(1 - \varphi_{12}^{(1)}) (w_{1r} \Omega_{0r} + w_{1\theta} \Omega_{0\theta}) I_3(|\mathbf{r}_1 - \mathbf{r}_{01}|)]; \\ & \frac{1}{2} \int_S \left( \frac{A_2(\theta_0)}{\pi^{1/2}} + \frac{1}{2} \frac{H_1}{\varphi_{12}^{(1)}} x_1 \left( \frac{m_1}{m_2} \right)^{1/2} \cos \theta_0 \right) ds \\ &= \pi^{-3/2} \int_{V_0} d\mathbf{r}_2 \int_{\omega_0} d\omega [\nu_2 I_2(|\mathbf{r}_2 - \mathbf{r}_{02}|) - 2(w_{2r} \Omega_{0r} + w_{2\theta} \Omega_{0\theta}) I_3(|\mathbf{r}_2 - \mathbf{r}_{02}|)].\end{aligned}\quad (2.2)$$

Here  $H_1 = (x_1 R_0 \gamma_{12})^{-1/2} (2kT/m_1)^{1/2}$  and  $V_0$  is the full space around the sphere.

The expressions for the diffusion force obtained from Eq. (1.16) with allowance for (1.14), (1.15), and (1.11) for Lorentzian (subscript  $L$ ) and Rayleigh (subscript  $R$ ) mixtures have the form

$$\begin{aligned}F_L &= n_{10} kT R_0 \left| \nabla x_1 \right|_\infty \left\{ -\frac{8\pi^{1/2}}{3} \frac{H_1}{\varphi_{12}^{(1)}} R_0^2 - \frac{1}{2} \int_S A_1(\theta_0) \cos \theta_0 dS - 2\pi^{-3/2} \frac{2kT}{m_1} \frac{1}{\gamma_{12}^2} \right. \\ & \times \left. \int_{V_0} d\mathbf{r}_1 \int_{\omega_0} d\omega \Omega_{0z} [\nu_1 I_3(|\mathbf{r}_1 - \mathbf{r}_{01}|) - 2(1 - \varphi_{12}^{(1)}) (w_{1r} \Omega_{0r} + w_{1\theta} \Omega_{0\theta}) I_4(|\mathbf{r}_1 - \mathbf{r}_{01}|)] \right\},\end{aligned}\quad (2.4)$$

$$F_R = n_{20}kTR_0 \left| \nabla x_1 \right|_{\infty} \left\{ \frac{8\pi^{1/2}}{3} x_1 \left( \frac{m_1}{m_2} \right)^{1/2} \frac{H_1}{\varphi_{12}^{(1)}} R_0^2 - \frac{1}{2} \int_S A_2(\theta_0) \cos \theta_0 dS - 2\pi^{-3/2} \frac{2kT}{m_2} \frac{1}{\gamma_{22}^2} \right. \\ \left. \times \int_{V_0} d\mathbf{r}_2 \int_{\omega_0} d\omega \Omega_{0Z} [\nu_2 I_3(|\mathbf{r}_2 - \mathbf{r}_{02}|) - 2(w_{2r}\Omega_{0r} + w_{2\theta}\Omega_{0\theta}) I_4(|\mathbf{r}_2 - \mathbf{r}_{02}|)] \right\}, \quad (2.5)$$

where  $dS = R_0^2 \sin \theta_0 d\theta_0 d\varphi_0$ ,  $|\mathbf{r}_{01}| = R_0(m_1/(2kT))^{1/2}\gamma_{12}$ , and  $|\mathbf{r}_{02}| = R_0(m_2/(2kT))^{1/2}\gamma_{22}$ .

As might be expected, for a Lorentzian mixture, the diffusion force is determined only by the macroscopic parameters only the first component, and for a Rayleigh mixture, it is determined only by the second component. This implies that to calculate  $F_L$ , it suffices to solve Eqs. (2.1) for  $\alpha = 1$  using Eq. (2.2). To calculate the diffusion force for a Rayleigh mixture  $F_R$ , it suffices to solve Eq. (2.1) for  $\alpha = 2$  using Eq. (2.3).

The system of integral equations (2.1) was solved by the Bubnov–Galerkin method, whose applicability to Fredholm integral equations of the second kind was discussed in [19]. The effectiveness of this method lies in the fact that it converges on the average, i.e., it allows one to calculate the diffusion force with specified accuracy, using only approximations of coordinate dependences of the gas density and velocity.

If the angular dependence of the macroscopic quantities is specified by a series in Legendre polynomials, then, by virtue of the orthogonality of the polynomials, expression (1.16) implies that only terms corresponding to first-order polynomials make a contribution to the diffusion force. Then, an angular dependences of the form  $\nu_\alpha \sim \cos \theta$ ,  $w_{\alpha r} \sim \cos \theta$ ,  $w_{\alpha \theta} \sim \sin \theta$ , and  $A_\alpha \sim \cos \theta_0$ , obtained in calculations of the diffusion force in the free-molecular [20] and hydrodynamic [6] regimes and satisfying the conservation laws, can be used for intermediate Knudsen numbers as well. It remains to approximate the dependence of the unknown macroparameters only on the radial coordinate  $r$ .

The perturbations of the gas macroparameters due to the presence of the particle should disappear at large distances from the particle. This condition and the macroscopic conservation laws are satisfied for the systems of basis functions  $\{r^{-2k}\}$  for perturbations of the partial densities  $\nu_\alpha$  and  $\{r^{-(2k-1)}\}$  for the velocities  $w_{\alpha r}$  and  $w_{\alpha \theta}$ , where  $k = 1, \dots, N$  ( $N$  is the approximation order).

The free terms of Eqs. (2.1) already contain accurate free-molecular values for the sought macroparameters. Therefore, specifying trial functions for  $\nu_\alpha$  and  $w_\alpha$  by the form of the hydrodynamic solution of the problem, one obtains fairly accurate results for the diffusion force over the entire range of Kn. One can show that the hydrodynamic limit [6] corresponds to the second approximation ( $N = 2$ ) of the Bubnov–Galerkin method. In this case, the approximating functions satisfying the continuity equations and equations of motions have the form

$$\nu_\alpha = C_1^\alpha \frac{R_\alpha^2}{r_\alpha^2} \cos \theta, \quad w_{\alpha r} = -\frac{R_\alpha}{r_\alpha} \left[ 1 - C_2^\alpha \left( 1 - \frac{R_\alpha^2}{r_\alpha^2} \right) \right] \cos \theta, \\ w_{\alpha \theta} = \frac{1}{2} \frac{R_\alpha}{r_\alpha} \left[ 1 - C_2^\alpha \left( 1 + \frac{R_\alpha^2}{r_\alpha^2} \right) \right] \sin \theta, \quad A_\alpha = C_3^\alpha \cos \theta_0, \quad (2.6)$$

where  $R_\alpha = |\mathbf{r}_{0\alpha}|$  and  $C_i^\alpha$  are unknown constants (in this case, the subscript  $\alpha = 1$  corresponds to the approximation of a Lorentzian mixture and the subscript  $\alpha = 2$  corresponds to a Rayleigh mixture).

When the problem is solved in a higher approximation ( $N = 3$ ) to study the rate of convergence of the Bubnov–Galerkin method, the volume of calculations increases considerably. Therefore, such a study was not performed. However, the experience of solving similar problems (see, e.g., [16, 17]) shows that the choice of trial functions in the form (2.6) ensures exact results in the Knudsen and hydrodynamic limits and gives an error less than 3% for intermediate Kn.

Substituting approximations (2.6) into the system of integral equations (2.1) and requiring that the expressions obtained be orthogonal to each of the basis functions (2.6), we obtain a system of algebraic equations that define the unknown constants  $C_i^\alpha$  in approximations (2.6):

$$\sum_{j=1}^3 \alpha_{ij} C_j^\alpha = \alpha_i \quad (i = 1, 2, 3). \quad (2.7)$$

Having determined the quantities  $C_i^\alpha$  by solving Eqs. (2.7) with allowance for expressions (2.4) and (2.5), we obtain the diffusion force for both models for the gas mixture:

$$F_L = n_{10}kT \left| \nabla x_1 \right|_{\infty} R_0 \left\{ -\frac{8\pi^{1/2}}{3} R_0 \left( \frac{2kT}{m_1} \right)^{1/2} \frac{1}{\nu_{12}^{(1)} x_1} - \frac{2}{3} \pi R_0^2 C_3^1 - \frac{2kT}{m_1} \frac{1}{\gamma_{12}^2} [C_1^1 \beta_1 + 2(1 - \varphi_{12}^{(1)}) (\beta_2' + C_2^1 \beta_2)] \right\}; \quad (2.8)$$

$$F_R = n_{20}kT \left| \nabla x_1 \right|_{\infty} R_0 \left\{ \frac{8\pi^{1/2}}{3} R_0 \left( \frac{2kT}{m_2} \right)^{1/2} \frac{1}{\nu_{12}^{(1)}} - \frac{2}{3} \pi R_0^2 C_3^2 - \frac{2kT}{m_2} \frac{1}{\gamma_{22}^2} [C_1^2 \beta_1 + 2(\beta_2' + C_2^2 \beta_2)] \right\}.$$

The expressions for the Galerkin coefficients  $\alpha_{ij}$  and  $\alpha_i$ , and the quantities  $\beta_i$  and  $\beta_i'$ , which depend on Knudsen number are cumbersome, and, therefore, are not given here. Calculating them at arbitrary Knudsen number is the most laborious part of the solution of the problem. We note that the computation error for the Galerkin coefficients do not exceed 0.5%.

**3. Discussion of Results.** The expressions for the force and rate of diffusiophoresis at large and small Knudsen numbers can be obtained by asymptotic expansions of the Galerkin coefficients. At  $\text{Kn} \gg 1$ , we have

$$F_L = -\frac{8\pi^{1/2}}{3} \left(1 + \frac{\pi}{8}\right) R_0^2 n_{20} (2kT)^{1/2} m_1^{1/2} D_{12} \left| \nabla x_1 \right|_{\infty} \left(1 - \frac{0.324}{\text{Kn}_L}\right), \quad (3.1)$$

$$F_R = \frac{8\pi^{1/2}}{3} \left(1 + \frac{\pi}{8}\right) R_0^2 n_{20} (2kT)^{1/2} m_1 m_2^{-1/2} D_{12} \left| \nabla x_1 \right|_{\infty} \left(1 - \frac{0.324}{\text{Kn}_R}\right), \quad (3.2)$$

where, according to the first Chapman–Enskog approximation [13], the interdiffusion coefficient is  $D_{12} = kT/(m_1 \nu_{12}^{(1)})$ . In the case of Lorentzian mixture ( $\text{Kn}_L$ ) and Rayleigh mixture ( $\text{Kn}_R$ ), the expressions for Knudsen numbers have the form  $\text{Kn} = \pi^{1/2}/(2R)$ . Here for solid spherical molecules, we have

$$R_L = \gamma_{12} \left( \frac{m_1}{2kT} \right)^{1/2} R_0 = \frac{16\pi^{1/2}}{5} n R_0 d_{12}^2, \quad R_R = \gamma_{22} \left( \frac{m_2}{2kT} \right)^{1/2} R_0 = \frac{16}{5} \left( \frac{\pi}{2} \right)^{1/2} n R_0 d_2^2.$$

For diffusion of the first component through the second fixed component, we have

$$R_{SD} = \frac{16\pi^{1/2}}{5} \frac{m_2^{1/2} (5/3 + m_2/m_1)}{(m_1 + m_2)^{3/2}} n R_0 d_{12}^2.$$

We note that the results (3.1) and (3.2) are new. For  $\text{Kn} \rightarrow \infty$ , they agree with the data of [1–4] for Rayleigh and Lorentzian mixtures.

Using the results of [16] for the drag force at  $\text{Kn} \gg 1$

$$F_F = \frac{16\pi^{1/2}}{3} \left(1 + \frac{\pi}{8}\right) R_0^2 n_{20} kT \left( \frac{m_2}{2kT} \right)^{1/2} \mathbf{V}_{\infty} \left(1 - \frac{0.324}{\text{Kn}_R}\right), \quad (3.3)$$

for the diffusiophoresis rate  $\mathbf{U}_D = -\mathbf{V}_{\infty}$ , we obtain the following relations:

$$U_L = -\left( \frac{m_1}{m_2} \right)^{1/2} D_{12} \left| \nabla x_1 \right|_{\infty} \left(1 - \frac{0.095}{\text{Kn}_L}\right), \quad U_R = \frac{m_1}{m_2} D_{12} \left| \nabla x_1 \right|_{\infty}. \quad (3.4)$$

We note that for  $\text{Kn} \rightarrow \infty$ , expressions (3.4) agree with the results of [20, 21] at  $x_1 \ll 1$  for the cases  $m_1/m_2 \ll 1$  and  $m_1/m_2 \gg 1$ . As shown by calculations of the diffusiophoresis force and rate over the entire range of Knudsen numbers (see Table 1), expressions (3.1), (3.2), and (3.4) can be used for  $\text{Kn} \geq 2$ , and the error in this case does not exceed 2–5%.

For the slip regime, by asymptotic expansion of the Galerkin coefficients in the small parameter  $\text{Kn} \ll 1$ , we also obtained expressions for the diffusiophoresis force and rate. In this case,

$$F_{L,R} = -6\pi\eta R_0 \sigma_{12}^{L,R} D_{12} \left| \nabla x_1 \right|_{\infty} \quad (3.5)$$

( $\eta$  is the viscosity of the gas mixture). For the hydrodynamic velocity of the mixture, the diffusion slip coefficients  $\sigma_{12}$  take the form

$$\sigma_{12}^L = \gamma_{22}/\gamma_{12}, \quad \sigma_{12}^R = -m_1/m_2, \quad (3.6)$$

and in the case of a Lorentzian mixture with molecules treated as solid spheres with effective diameters  $d_1$  and  $d_2$ , we have  $\gamma_{22}/\gamma_{12} = (m_1/(2m_2))^{1/2} (d_2/d_{12})^2$ , where  $d_{12} = (d_1 + d_2)/2$ .

We note that expressions (3.6) result from gas-kinetic analysis and agree with the expressions given in [6], provided that  $x_1 \ll 1$  and passage to the limit for molecular weights is performed.

TABLE 1

Calculated Diffusiophoresis Force and Rate  
Normalized to Free-Molecular Values for Intermediate Knudsen Numbers

$R = (\pi^{1/2}/2)\text{Kn}^{-1}$	$F_L^*$	$U_L^* (d_1 \approx d_2)$	$F_R^*$	$U_R^*$
10	0.129	1.000	0.127	0.977
9	0.142	1.000	0.139	0.979
8	0.157	1.000	0.154	0.975
7	0.177	1.000	0.174	0.976
6	0.202	1.000	0.199	0.980
5	0.234	0.996	0.236	1.000
4	0.280	1.000	0.281	0.996
3	0.347	1.000	0.344	0.986
2.5	0.394	1.000	0.390	0.985
2	0.455	0.998	0.451	0.989
1.75	0.493	1.000	0.490	0.994
1.5	0.538	1.000	0.534	0.994
1.25	0.589	0.998	0.585	0.997
1.0	0.651	1.000	0.652	1.010
0.8	0.709	1.000	0.705	1.000
0.75	0.724	1.000	0.725	1.010
0.6	0.774	1.001	0.769	0.999
0.5	0.809	1.000	0.804	0.998
0.4	0.845	0.998	0.841	0.995
0.25	0.905	1.000	0.907	1.000
0.2	0.925	1.000	0.923	0.995
0.1	0.963	1.000	0.962	0.992
0.08	0.971	1.000	0.968	0.990
0.075	0.973	1.000	0.970	0.991
0.06	0.978	1.000	0.975	0.990
0.05	0.982	0.999	0.981	0.993

Using the Stokes formula  $F_F = 6\pi\eta\mathbf{V}_\infty R_0$  for the drag force at  $\text{Kn} \ll 1$ , we obtain the following relations for the diffusiophoresis rate:

$$U_{L,R} = -\sigma_{12}^{L,R} D_{12} \left| \nabla x_1 \right|_\infty. \quad (3.7)$$

From relations (3.1)–(3.7) it follows that for Lorentzian mixtures, the diffusiophoresis force and rate are in opposition to the concentration gradient, for Rayleigh mixtures, they are directed along the concentration gradient of the first component (because  $\sigma_{12}^R < 0$ ).

At intermediate Knudsen numbers, we performed numerical calculations of the diffusion force normalized to the free-molecular value:

$$F_{L,R}^*(\text{Kn}_{L,R}) = F_{L,R}(\text{Kn}_{L,R})/F_{L,R}(\text{Kn}_{L,R} \rightarrow \infty).$$

Then, we calculated the normalized rate of diffusiophoresis

$$U_{L,R}^*(\text{Kn}_{L,R}) = F_{L,R}^*(\text{Kn}_{L,R})/F_F^*(\text{Kn}_{L,R}),$$

where  $F_F^*(\text{Kn}_{L,R})$  is the drag force normalized to the free-molecular value [16]. The calculation results are given in Table 1.

Figure 2 shows the dependences of the diffusiophoresis force and rate on  $\text{Kn}_L$  for a Lorentzian mixture. For a Rayleigh mixture, the results are identical if  $\text{Kn}_L$  replaced by  $\text{Kn}_R$ . From the calculations it follows that the normalized rate of diffusiophoresis  $U_{L,R}^*$  practically does not depend on  $\text{Kn}$ . This conclusion agrees qualitatively with the results of the method of “giant molecules” [10]. The indistinct minimum for the diffusiophoresis rate at  $\text{Kn} \approx 0.1$ – $1.0$ , noted in [10] for equimolar mixtures, was not revealed within the calculation error.

Let us consider the particular case of diffusion of one component of the mixture through the second fixed component. This scheme was implemented in experimental studies of the diffusiophoresis rate [4, 11, 12]. It can be shown that for diffusion of one component of low concentration ( $x_1 \ll 1$ ) through the other fixed component at any



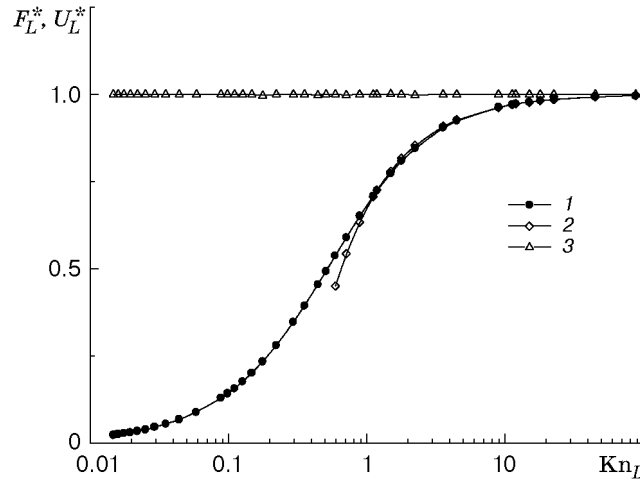


Fig. 2. Dependences of the normalized force  $F_L^*$  [1 by Eq. (2.8) and 2 by Eq. (3.1)] and rate of diffusiophoresis  $U_L^*$  (3) on  $\text{Kn}_L$  for a Lorentzian mixture.

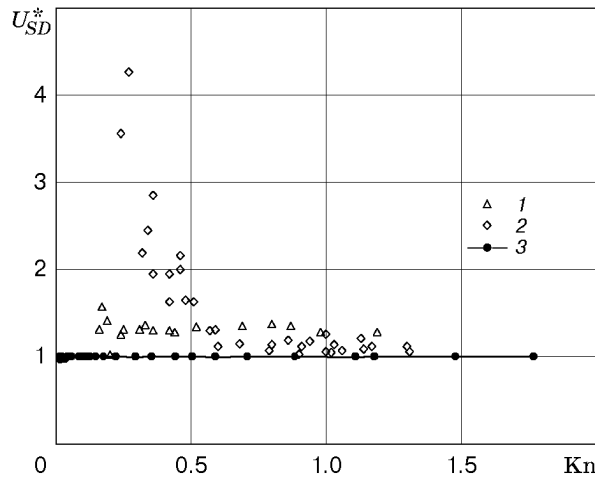


Fig. 3. Normalized rate of diffusiophoresis  $U_{SD}^*$  versus  $\text{Kn}$  for diffusion of one component through the second fixed component: points 1 and 2 refer to experimental data of [11] and [12], respectively, and points 3 refer to numerical calculations.

ratios of molecular weights, the form of the kinetic equation (2.1) for the first component does not change, only the expressions for the frequencies  $\nu_{\alpha\beta}^{(k)}$  change, and the kinetic equation for the second component does not contribute to the diffusion force. Thus, for this diffusion scheme, one can use the solution of the problem for a Lorentzian mixture but with different values of the frequencies  $\nu_{\alpha\beta}^{(k)}$  [14].

In the free-molecular limit, we obtain

$$F_{SD} = -(8\pi^{1/2}/3)(1 + \pi/8)R_0^2 n(2kT)^{1/2} m_1^{1/2} D_{12} \left| \nabla x_1 \right|_{\infty}, \quad U_{SD} = -(m_1/m_2)^{1/2} D_{12} \left| \nabla x_1 \right|_{\infty}, \quad (3.8)$$

which agrees with the result (3.1) at  $\text{Kn} \rightarrow \infty$  for a Lorentzian mixture in the case of constant-pressure diffusion. We note that relations (3.8) follow from the results of [11] at  $x_1 \ll 1$  and any ratio of molecular weights.

In the slip regime at  $\text{Kn} \ll 1$ , we have  $F_{SD} = -6\pi\eta R_0 \sigma_{12} D_{12} \left| \nabla x_1 \right|_{\infty}$  and  $U_{SD} = -\sigma_{12} D_{12} \left| \nabla x_1 \right|_{\infty}$ , where  $\sigma_{12} = \gamma_{22}/\gamma_{12}$ . For molecules treated as solid spheres at an arbitrary ratio of molecular weights, we have

$$\frac{\gamma_{22}}{\gamma_{12}} = \left( \frac{d_2}{d_{12}} \right)^2 \frac{(m_1 + m_2)^{3/2}}{(2m_1)^{1/2} m_2} \frac{1}{m_2/m_1 + 5/3}.$$

At intermediate Knudsen numbers, the calculated values of the diffusiophoresis force and rate agree with the results for the model of a Lorentzian mixture in the constant-pressure diffusion scheme if  $\text{Kn}_L$  is replaced by  $\text{Kn}_{SD}$  (see Table 1).

A comparison of theoretical and experimental data is presented in Fig. 3. The figure shows measured diffusiophoresis rates for droplets of M300 silicone oil in the case of diffusion of water vapor in fixed nitrogen ( $m_1/m_2 \approx 0.64$ ) [11] and for droplets of liquid petrolatum in the case of diffusion of water vapor in air ( $m_1/m_2 \approx 0.62$ ) [12]. In these experiments, the theoretical condition  $x_1 \ll 1$  was used. Calculated values of the normalized rate of diffusiophoresis  $U_D^*$  are also given here. The Knudsen number  $\text{Kn} = l_2/R_0$  is determined from the average free path of molecules of the fixed component  $l_2$ . The theoretical results are in good agreement with experiments. The abnormal increase in the normalized rate at  $\text{Kn} < 0.5$  in the experiment of [12], in our opinion, is due to the fact that the jet procedure does not distinguish between diffusion and convective transport of particles at small Knudsen numbers (see, e.g., [22]). The results of investigation [11] using a Millikan capacitor appear to be free of this disadvantage [22]. The systematic 10–20% excess of experimental data above calculation results over the entire explored range of Knudsen numbers can be attributed to incomplete accommodation of the momentum of molecules on the particle surface, which was ignored in theory.

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