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Photophoresis of a fine particle in a selectively excited gas

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Motion in a binary gas mixture of a fine particle affected by resonant optical radiation is considered. The Doppler effect leads to the velocity-selective absorption of the traveling light wave by molecules of one of the gas components. Radiation transfers the absorbing molecules from the ground state to excited ones. As a result, the kinetic cross section and accommodation coefficient of molecules, which have absorbed radiation, change. Maxwellian distribution for the absorbing gas molecules becomes distorted and the aerosol particle begins to be influenced by a force. This photophoretic force and velocity of the photophoresis are calculated by taking both the optical and kinetic characteristics of the gas molecules into account.

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I. INTRODUCTION

Phenomena related to the effect of optical radiation on aerosol particles of submicron size are important for astrophysics, physics, and chemistry of the atmosphere, especially for the laser monitoring of the atmosphere. Motion of aerosol particles in the field of optical radiation is one of the major processes governing the time needed for the aerodisperse system to be cleared up.

Consider a fine aerosol particle, which is influenced by optical radiation. This particle absorbs light nonuniformly. It is well known that a force on acting the particle can be considered as resulting from interactions of the gas molecules with a nonuniformly heated particle surface. The light interacts with the particle, but it does not affect the surrounding gas (so-called radiometric photophoresis). The kinetic theory of radiometric photophoresis at arbitrary Knudsen number has been presented in Ref. [1].

On the other hand, the velocity-selective excitation of the gas molecules can be the other mechanism leading to the photophoresis. Let us assume that radiation propagates in the binary gas mixture and excites one of the components. The Doppler effect leads to the velocity-selective absorption of the radiation by the gas molecules. The effective resonant velocity interval is determined by the following condition: $\mathbf{k}\Delta\mathbf{v}\sim\Gamma$, where $\mathbf{k}$ is the wave vector and Γ is the homogeneous width of absorption line of the molecular transition. Radiation transfers absorbing molecules from the ground state to the excited ones. The kinetic cross section of excited molecules differs from that for molecules in the ground state. Consequently, the Maxwellian distribution for the absorbing gas molecules becomes distorted. As a result, the light-induced drift and energy flux take place in the surrounding gas [2]. Difference in the kinetic cross sections is one of the reasons for the so-called bulk photophoresis. However, there exist another one. In the case, when scattering of the excited molecules from the particle surface differs from that for molecules in the ground state, a force acting upon the particle appears (so-called surface photophoresis).

Theory of the resonant photophoresis of a particle in a pure light-absorbing gas has been presented in Refs. [3,4]. In order to obtain the velocity distribution functions for excited and ground-state molecules, Derjaguin and Roldughin [3] used the Grad momentum technique [5]. The obtained distributions do not take into account significant singularities within the interval of the resonant velocities ($\Delta\mathbf{v}\sim\Gamma/\mathbf{k}$). The assumption that far from the particle surface the surrounding gas is spatially homogeneous was applied in Ref. [4]. In Ref. [4] only the surface mechanism of photophoresis has been considered. This mechanism is caused by the difference in the momentum accommodation coefficients of the molecules in the excited and ground states. The influence of the bulk photophoresis in Ref. [4] was not accounted for.

In the case where an aerosol particle is suspended in the mixture of the light-absorbing and nonabsorbing buffer gases, the magnitude of the photophoretic force depends also on the mixture composition, molecular masses, and kinetic cross sections.

In this paper, the photophoresis of an aerosol particle suspended in the gas mixture, where molecules of one of the components are velocity-selectively excited by resonant optical radiation, is considered. It is assumed that the aerosol particle either does not absorb light or absorbs light uniformly. In the paper, a free-molecular regime (the aerosol particle is assumed to be small compared to the mean free path of gas molecules) is investigated.

II. STATEMENT OF THE PROBLEM

Consider a spherical aerosol particle of radius r_0 suspended in a binary gas mixture, which is influenced by a uniform monochromatic radiation.

The light wave propagates along the positive z axis (Fig. 1). We assume that molecules of one of the gas components absorb radiation in the electronic or vibrational-rotational transition from the ground state n to the excited state m. The radiation frequency ω is slightly detuned from the center

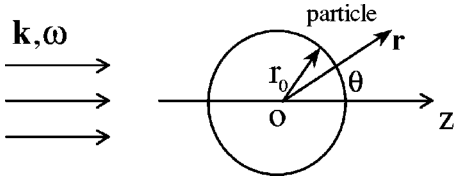

FIG. 1. Geometry of the problem; $\mathbf{k}$ is the wave vector, ω is the frequency of radiation.

of the absorption line at ω_{mn}, i.e., $\Omega=\omega-\omega_{mn}$, $(|\Omega| \ll \omega,\omega_{mn})$.

Due to the Doppler effect, the radiation is absorbed selectively by molecules that have velocities around $v_r=\Omega/k$, where k is the magnitude of the wave vector and v_r the light-selected velocity component along the propagation direction of the light. Molecules that have absorbed radiation change the kinetic cross section and accommodation coefficient. Thus, the gas phase can be interpreted as a ternary mixture consisting of the excited and nonexcited components and the buffer gas. The excited and unexcited molecules have equal masses m_1 but the effective diameter of molecules in the ground state, d_n, differs from that in the excited state, d_m. Stimulated transitions and radiative decay of the excited levels lead to the exchange of molecules between excited and nonexcited components. The buffer-gas molecules have the mass of m_2 and effective diameter of d_2.

Resonant radiation disturbs the equilibrium in the gas. In the case of finite detuning $\Omega \neq 0$ this stimulates the drift of the light-absorbing gas in parallel to the wave-vector direction [2], whereas the buffer gas moves in the opposite direction. These macroscopic fluxes experience different drags when flowing around the particle because the ground-state molecules, excited-state molecules, and buffer-gas molecules interact with the particle surface differently and they also have different transport characteristics and masses. Consequently, the gas transfers an uncompensated momentum to the particle. This means that there is a force acting upon the particle. This force is directed in parallel to the z axis that can be explained by the symmetry of the problem (see Fig. 1).

Knowing the velocity distribution functions for molecules in the excited state, f_m, in the ground-state, f_n, and that for buffer-gas molecules, f_2, one can calculate the photophoretic force as

$$F_R=2\pi r_0^2\int_0^{\pi}\sin\,\theta\,d\theta\sum_{i=m,n,2} m_i\int v_r v_z f_i\,d\mathbf{v}. \tag{1}$$

Here the subscripts 1 and 2 designate quantities that refer to the light-absorbing gas and buffer gas, respectively; the subscripts m and n designate quantities that refer to molecules in the excited and in the ground state.

For two-level molecules of light-absorbing gas (n and m), the velocity distribution functions are described by the following kinetic equations [6]:

$$\frac{\partial f_n}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla} f_n=\frac{1}{2}\Gamma_m\kappa(\mathbf{v})(f_m-f_n)+\Gamma_m f_m+S_n, \tag{2}$$

$$\frac{\partial f_m}{\partial t}+\mathbf{v}\cdot\nabla f_m=-\frac{1}{2}\Gamma_m\kappa(\mathbf{v})(f_m-f_n)-\Gamma_m f_m+S_m, \tag{3}$$

$$\frac{\partial f_2}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla} f_2=S_2. \tag{4}$$

Here

$$S_i=S_{im}+S_{in}+S_{i2},\quad i=m,n,2,$$

$$\kappa(\mathbf{v})=\frac{4|G_{mn}|^2\Gamma}{\Gamma_m[\Gamma^2+(\Omega-\mathbf{k}\cdot\mathbf{v})^2]},\quad G_{mn}=\frac{d_{mn}E_0}{2\hbar}, \tag{5}$$

where Γ_m is the rate of radiative decay of the excited level, $\kappa(\mathbf{v})$ is the absorption probability per unit time for molecules with given velocity $\mathbf{v}$, d_{mn} is the dipole matrix element of $m-n$ transition, E_0 is the amplitude of the electrical field in the light wave, G_{mn} is the Rabi frequency, S_{ij} are the Boltzmann collision integrals for molecules of the ith and jth species, and $\hbar$ is the Planck constant.

The boundary conditions associated with Eqs. (2)–(4) are defined by the distribution functions $f_i^+(\mathbf{r}_0,\mathbf{v})$ $(i=m,n,2)$ for molecules reflected from the particle surface. In general, the particle surface temperature T_s differs from the equilibrium temperature in the gaseous media, T_0, due to the light absorption. We assume that the particle either does not absorb light at all or absorbs it homogeneously. In both cases the particle surface temperature is uniform and, consequently, the radiometric photophoresis does not occur.

We assume that the interaction of molecules of species i with the particle surface can be described by Maxwell's model. Neglecting the inelastic collisions of the molecules with the particle surface, one gets the boundary conditions in the following form

$$f_i^+(\mathbf{r}_0,\mathbf{v})=\varepsilon_i f_i^s+(1-\varepsilon_i)f_i^-[\mathbf{v}-2(\mathbf{v}\cdot\mathbf{n})\mathbf{n}],$$

$$i=m,n,2\ \ (\mathbf{v}\cdot\mathbf{n})>0, \tag{6}$$

$$f_i^s=n_{is}\left(\frac{m_i}{2\pi k_b T_0}\right)^{3/2}\exp\left(-\frac{v^2}{\overline{v}_i^2}\right),$$

$$\overline{v_i}=\left(\frac{2k_bT_0}{m_i}\right)^{1/2},$$

where $\mathbf{n}$ is the outer normal to the particle surface, ε_i is the fraction of molecules i which are reflected diffusely, f_i^+ and f_i^- are the velocity distribution functions for molecules, reflected from and incident at the surface, and k_b is the Boltzmann constant. The unknown number densities n_{is} are determined from the condition of impermeability of the particle surface to the gas molecules

$$N_i^+=|N_i^-|,\quad i=m,n,2. \tag{7}$$

Here N_i^+ and N_i^- are the number of molecules, reflected from and incident at the particle surface per unit time, respectively. These quantities can be expressed as

$$N_i^+=\int_{(\mathbf{v}\cdot\mathbf{n})>0} v_r f_i^+(\mathbf{r}_0,\mathbf{v})\ \ d\mathbf{v},$$

$$|N_i^-|=\int_{(\mathbf{v}\cdot\mathbf{n})<0}|v_r|f_i^-(\mathbf{r}_0,\mathbf{v})d\mathbf{v}. \tag{8}$$

The distribution functions for the incident molecules, f_i^-, are given in Eqs. (2)–(4).

We examine the case of small values of $\kappa(\mathbf{v})$ that is quite typical for vibrational-rotational transitions and also for electronic transitions at low radiation intensity. In this case the system is quite near the equilibrium and, thus, the distribution functions can be written in the form of the perturbed Maxwellian distributions

$$f_i(\mathbf{v})=f_{i0}[1+h_i(\mathbf{v})], \tag{9}$$

$$f_{i0}=n_i\left(\frac{m_i}{2\pi k_b T_0}\right)^{3/2}\exp\left(\frac{m_i v^2}{2k_b T_0}\right),$$

where $h_i(\mathbf{v})$ is the disturbance function and n_i is the equilibrium number density of molecules of species i.

In the steady-state regime the distribution functions do not alter with time and, consequently, the time derivatives in the kinetic equations (2)–(4) can be neglected.

We consider the free-molecular regime where the mean free path of molecules is large compared to the particle radius. In this case, the perturbation of the distribution function for molecules incident upon the particle surface due to the interaction with reflected molecules can be neglected. Therefore, the distribution functions of incident molecules are the same as those in the case when the particle is absent. We also assume that the radiation intensity is independent of the coordinates and the transverse size of the light beam is big compared to the mean free path of the gas molecules. At such conditions the distribution functions of the incident molecules, f_i^-, are spatially homogeneous. Hence, the spatial derivatives in Eqs. (2)–(4) for the functions f_i^- can be neglected. It is important to note that the full distribution functions depend on coordinates.

In the free-molecular regime, the influence of the "shadow" formed by the aerosol particle is negligible because only a small part of molecules is in the "shaded" area.

Accounting for the above assumptions, one gets the linearized equations (2)–(4) for the disturbance functions h_i of incident molecules in the following form

$$\frac{1}{2}\Gamma_m\kappa(\mathbf{v})\left(\frac{n_n}{n_m}-1\right)-\Gamma_m(1+h_m)+L_{mm}+L_{mn}+L_{m2}=0, \tag{10}$$

$$-\frac{1}{2}\Gamma_m\kappa(\mathbf{v})\left(1-\frac{n_m}{n_n}\right)+\frac{n_m}{n_n}\Gamma_m(1+h_m)+L_{nm}+L_{nn}+L_{n2}=0, \tag{11}$$

$$L_{2m}+L_{2n}+L_{22}=0. \tag{12}$$

where L_{ij} is the linearized collision integral.

III. DISTRIBUTION FUNCTIONS

Since only elastic collisions between molecules are considered, we can use the linearized collision integral L_{ij} of third order developed by McCormack [7]:

$$L_{ij}=-\gamma_{ij}h_i+A_{ij}, \tag{13}$$

where γ_{ij} is the effective collision frequency between the molecules of the i-th and j-th species; A_{ij} is the linearized operator of inverse collisions.

In the expression for A_{ij} we have to take into account that the mean free path of the molecules is large compared to the particle radius. This means that the particle does not perturb the gaseous media. The kinetic equations (10)–(12) describe the distribution functions, which depends only on the interaction of the molecule with each other and with light. Far from the particle surface the gas and energy fluxes are directed in parallel to the z axis and the tangential stresses in the gas are absent. The light-induced anisotropy of the partial pressures [6,8] contributes nothing to the photophoretic force F_R (1)and, consequently, terms with the stress tensor can be excluded from the expression for operator A_{ij}.

Temperature of the gas components is different due to the light-induced cooling and heating [6,8,9], but its distribution is spatially homogeneous [9]. Hence, the terms accounting for the difference in the temperatures of the components contribute nothing to the photophoretic force and they can be excluded from the expression for A_{ij}.

Thus, the operator A_{ij} can be written as [7]

$$\begin{aligned}A_{ij}={}&2c_{iz}[\gamma_{ij}u_i-(u_i-\sqrt{m_i/m_j}\;u_j)\nu_{ij}^{(1)}\\&-(H_i-(m_j/m_i)^{3/2}H_j)\nu_{ij}^{(2)}]+\frac{8}{5}\;c_{iz}\left(c_i^2-\frac{5}{2}\right)\\&\times\left[(\gamma_{ij}-\nu_{ij}^{(5)})H_i+\nu_{ij}^{(6)}H_j-\frac{5}{8}\;(u_i-\sqrt{m_i/m_j}\;u_j)\nu_{ij}^{(2)}\right],\end{aligned} \tag{14}$$

where

$$u_i=\frac{U_i}{\overline{v}_i}=\frac{1}{\pi^{3/2}}\int c_{iz}h_i\exp(-c_i^2)d\mathbf{c}_i, \tag{15}$$

$$\mathbf{c}_i=\frac{\mathbf{v}_i}{\overline{v}_i},\quad i,j=m,n,2,$$

$$\begin{aligned}H_i&=\frac{1}{2\overline{v}_i p_{i0}}\left(q_i-\frac{5}{2}\;\frac{k_bT_0}{m_i}\;J_i\right)\\&=\frac{1}{2\pi^{3/2}}\int c_{iz}\left(c_i^2-\frac{5}{2}\right)h_i\exp(-c_i^2)d\mathbf{c}_i.\end{aligned} \tag{16}$$

Here U_i is the velocity of component i, q_i is the heat flux of component i, J_i is the diffusion flux, and p_{i0} is the equilibrium partial pressure. The expressions for the rates $\nu_{ij}^{(k)}$ are given in Appendix A.

The solution of Eqs. (10)–(12), taking account of Eqs. (13) and (14), has the form

$$h_m^-=\frac{\Gamma_m}{\Gamma_m+\gamma_m}\;\left(\frac{n_n}{2n_m}\;\kappa(\mathbf{v})-1+\frac{A_m}{\Gamma_m}\right), \tag{17}$$

$$h_n^- = \frac{\Gamma_m}{\Gamma_m+\gamma_m}\,\frac{\gamma_m}{\gamma_n}\left(-\frac{1}{2}\,\kappa(\mathbf{v})+\frac{n_m}{n_n}\right)+\frac{\Gamma_m}{\Gamma_m+\gamma_m}\,\frac{n_m}{n_n}\,\frac{A_m}{\gamma_n}+\frac{A_n}{\gamma_n}, \tag{18}$$

$$h_2^- = \frac{A_2}{\gamma_2}, \tag{19}$$

where the superscript − refers to disturbance function for the incident molecules. The following designations have been used:

$$A_i = \sum_{j=m,n,2} A_{ij}, \quad \gamma_i = \gamma_{im}+\gamma_{in}+\gamma_{i2} \quad (i=m,n,2), \tag{20}$$

where γ_i is the effective collision frequency for molecules of species i.

The unknown macroscopic quantities u_i and H_i in Eqs. (17)–(19) can be calculated using Eqs. (15) and (16). This theory is linear in $\kappa(\mathbf{v})$. Therefore we can assume that $n_m \ll n_n$, i.e. $n_n \approx n_1$. In addition, in Eq. (14) we can neglect small terms of second order (of the thermal diffusion order) that are proportional to the frequency $\nu_{ij}^{(2)}$.

Far from the particle surface we have

$$u_m = \frac{\Gamma_m}{\Gamma_m+\nu_{mn}^{(1)}+\nu_{m2}^{(1)}}\,\frac{n_1}{n_m}\,\frac{\kappa_0}{\pi^{3/2}}, \tag{21}$$

$$\kappa_0 = \int c_{1z}\kappa(\mathbf{v})\exp(-c_1^2)\,d\mathbf{c}_1 .$$

$$H_m = \frac{\Gamma_m}{\Gamma_m+\nu_{mn}^{(5)}+\nu_{m2}^{(5)}}\,\frac{n_1}{n_m}\,\frac{\kappa_1}{4\pi^{3/2}}, \tag{22}$$

$$\kappa_1 = \int c_{1z}\left(c_1^2-\frac{5}{2}\right)\kappa(\mathbf{v})\exp(-c_1^2)\,d\mathbf{c}_1 .$$

The quantities κ_0 and κ_1, which depend on the detuning parameter $x=\Omega/k\overline{v_1}$ and broadening parameter $y=\Gamma/k\overline{v_1}$, can be expressed in a simple form in the case of inhomogeneous ($y\ll 1$) and homogeneous ($y \gg 1$) spectral line broadenings. The numerical calculation has been carried out for the intermediate values of y (see Appendix B).

The dimensionless drift velocity of the light-absorbing gas far from the particle surface is given by

$$u_1 = \frac{1}{n_1}\,(n_n u_n + n_m u_m) = \frac{n_m u_m}{n_1}\,\frac{n_2}{n_2+(m_1/m_2)^{3/2}n_1}\,\frac{\nu_{n2}^{(1)}-\nu_{m2}^{(1)}}{\nu_{n2}^{(1)}}. \tag{23}$$

Applying momentum conservation law to the gas mixture, one obtains the expression for the dimensionless velocity of the buffer gas,

$$u_2 = -\left(\frac{m_1}{m_2}\right)^{1/2}\frac{n_1}{n_2}\,u_1 . \tag{24}$$

For H_i we easily get

$$H_1 = \frac{\lambda_2}{\lambda_n\lambda_2-\nu_{n2}^{(6)}\nu_{2n}^{(6)}}\,\frac{n_m H_m}{n_1}\left(\Delta\nu-\frac{\nu_{2n}^{(6)}}{\lambda_2}(\nu_{n2}^{(6)}-\nu_{m2}^{(6)})\right), \tag{25}$$

$$H_2 = -\frac{\nu_{2n}^{(6)}}{\lambda_2}\left(H_1-\frac{n_m H_m}{n_1}\,\frac{\nu_{n2}^{(6)}-\nu_{m2}^{(6)}}{\nu_{n2}^{(6)}}\right), \tag{26}$$

where

$$\lambda_n = \nu_{2n}^{(5)}+\nu_{nn}^{(5)}-\nu_{nn}^{(6)}, \quad \lambda_2 = \nu_{2n}^{(5)}+\nu_{22}^{(5)}-\nu_{22}^{(6)},$$

$$\Delta\nu = (\nu_{n2}^{(5)}-\nu_{m2}^{(5)})+(\nu_{nn}^{(5)}-\nu_{mn}^{(5)})+(\nu_{mn}^{(6)}-\nu_{nn}^{(6)}).$$

For the gas mixture as a whole we have

$$H = \frac{n_1H_1+n_2H_2}{n}, \quad n=n_1+n_2 . \tag{27}$$

Thus, Eqs. (9) and (17)–(26) completely determine the velocity distribution functions of molecules incident upon the particle surface.

After the linearization of boundary conditions (6) was completed we obtain the disturbance functions for reflected molecules,

$$h_i^+ = \frac{n_{is}-n_i}{n_i}\,\varepsilon_i+(1-\varepsilon_i)h_i^-(-c_{ir},c_{i\theta},c_{i\varphi}). \tag{28}$$

Thus, for the disturbance functions on the particle surface we have

$$h_i(\mathbf{r}_0,\mathbf{c}_i) = \begin{cases} h_i^+(\mathbf{r}_0,\mathbf{c}_i) & (\mathbf{c}_i\cdot\mathbf{n})>0 \\ h_i^-(\mathbf{r}_0,\mathbf{c}_i) & (\mathbf{c}_i\cdot\mathbf{n})<0. \end{cases} \tag{29}$$

IV. FORCE AND VELOCITY OF PHOTOPHORESIS

Making use of Eq. (1) and applying the distribution functions given by Eqs. (9), (17)–(19), and (28), we obtain an expression for the photophoretic force

$$F_R = 4\pi r_0^2 p_1\left(G_s\Delta\varepsilon+G_\gamma\frac{\Delta\gamma}{\gamma_n}+G_u u_1+G_H H\right). \tag{30}$$

Here

$$G_s = -\frac{\pi^{1/2}}{6}\,\frac{n_m}{n_1}\,u_m, \quad G_H = \frac{8}{15\pi^{1/2}}\,\frac{n}{n_1}, \tag{31}$$

$$G_\gamma = -\frac{\Gamma_m}{2\pi^{1/2}(\Gamma_m+\gamma_m)}\left(\frac{10}{3}\,\kappa_0+\frac{16}{15}\,\kappa_1+\frac{\overline{\kappa_2}}{\pi}\right),$$

$$G_u = -\frac{1}{6\pi^{1/2}}\left\{ 20\left[\left(\frac{m_1}{m_2}\right)^{1/2} - 1\right] + \pi\left[\left(\frac{m_1}{m_2}\right)^{1/2} \pi\varepsilon_2 - 1\right]\right\},$$

$$\overline{\kappa_2} = \int_0^{\pi} \sin\theta \, d\theta \int_{c_{1r}<0} c_{1r} c_{1z} \kappa(\mathbf{v}) \exp(-c_1^2) \, d\mathbf{c}_1, \quad (32)$$

$$\Delta\varepsilon = \varepsilon_n - \varepsilon_m, \quad \Delta\gamma = \gamma_n - \gamma_m, \quad p_1 = n_1 k_b T_0.$$

The quantity $\overline{\kappa_2}$ is given as a function of parameters $x = \Omega/(k\overline{v_1})$ and $y = \Gamma/(k\overline{v_1})$ in Appendix B.

In Eq. (29), the kinetic coefficient G_s characterizes the surface mechanism of photophoresis related to the difference in the accommodation coefficients for excited and unexcited molecules of the absorbing gas.

The kinetic coefficient G_γ describes the contribution of the difference in the collision frequencies between excited and unexcited molecules. Excitation of molecules leads to change in their effective diameter or the mean free path. On the other hand, difference in the mean free paths of molecules in the excited and ground state leads to a difference in drags for fluxes of the gas components when flowing around the particle. As a result, a frequency mechanism of photophoresis arises.

The third and fourth terms in the expression (29), which are proportional to the drift velocity of absorbing gas and to the heat flux, are also associated with the difference in the collision frequencies of molecules in the excited and ground states. However, numerical estimations show that the contribution of the fourth term in Eq. (29) to the photophoretic force does not exceed 3% in all cases studied, and it may be as small as $< 1\%$ in the case of low concentrations of the buffer gas (for $n_2 \ll n_1$).

Particle, moving in the gas, are also affected by the drag $\mathbf{F}_c$. Therefore the velocity of the uniform motion of the particle, U_f, is determined from the following condition:

$$\mathbf{F}_R + \mathbf{F}_c = 0. \quad (33)$$

The drag in the free-molecular regime for the low concentration of excited molecules, $n_m \ll n_n$, is [10]

$$\mathbf{F}_c = -\frac{8\pi^{1/2}}{3} r_0^2 m_1 n_1 \overline{v_1} \alpha \mathbf{U}_f, \quad (34)$$

$$\alpha = 1 + \varepsilon_n \frac{8}{\pi} + \frac{n_2}{n_1}\left(\frac{m_2}{m_1}\right)^{1/2}\left(1 + \varepsilon_2 \frac{\pi}{8}\right).$$

Thus, the photophoretic velocity of the particle with respect to the mass center of the gas mixture is expressed as

$$U_f = \frac{3\pi^{1/2}}{4\alpha} \; \overline{v_1}\left(G_s \Delta\varepsilon + G_\gamma \frac{\Delta\gamma}{\gamma_n} + G_u u_1 + G_H H\right). \quad (35)$$

We choose effective collision rates in the form of $\gamma_{ij} = \nu_{ij}^{(1)}$. In addition, we assume that the interacting molecules are hard elastic spheres and the effective interaction radii of molecules in the excited state, d_{m2}, and ground state, d_{n2}, where the buffer-gas molecules are commensurate, i.e., $|d_{n2} - d_{m2}|/d_{n2} \ll 1$. In this case the expression (30) for the photophoretic force can be rewritten as

$$F_R = 4\pi r_0^2 p_1 \left(G_s \Delta\varepsilon + G_d \frac{\Delta d}{d_n}\right), \quad (36)$$

where

$$G_s = -\frac{\Gamma_m}{\Gamma_m + \gamma_m} \; \frac{\kappa_0}{6\pi}, \quad (37)$$

$$G_d = A G_\gamma + G_u \; \frac{\Gamma_m}{\Gamma_m + \gamma_m} \; \frac{n_2 d_n / d_{n2}}{n_2 + (m_1/m_2)^{3/2} n_1} \; \frac{\kappa_0}{\pi^{3/2}},$$

$$A = \frac{(m_1/2)^{1/2} n_1 d_n^2 + m_{12}^{1/2} n_2 d_n d_{n2}}{(m_1/2)^{1/2} n_1 d_n^2 + m_{12}^{1/2} n_2 d_{n2}^2},$$

$$d_{ij} = \frac{1}{2}(d_i + d_j), \quad \Delta d = d_n - d_m, \quad m_{12} = \frac{m_1 m_2}{m_1 + m_2}.$$

The second term in parentheses in Eq. (36) characterizes the bulk mechanism of photophoresis, which is related to the difference in the effective diameters of the excited and unexcited molecules.

The particle velocity is described by

$$U_f = \overline{v_1}\left(\mu_s \Delta\varepsilon + \mu_d \; \frac{\Delta d}{d_n}\right), \quad (38)$$

where μ_s and μ_d are the kinetic coefficients characterizing the surface mechanism and the bulk mechanism of photophoretic velocity, respectively,

$$\mu_s = \frac{3\pi^{1/2}}{4\alpha} G_s, \quad \mu_d = \frac{3\pi^{1/2}}{4\alpha} G_d. \quad (39)$$

Expressions for the kinetic coefficients G_s and G_d may be considerably simplified in the cases of inhomogeneous and homogeneous broadening of the absorption line.

Inhomogeneous broadening ($y \ll 1$) is typical for rarefied gases. In this case we obtain

$$G_s = -\frac{2\pi |G_{mn}|^2}{3(\Gamma_m + \gamma_m) k\overline{v_1}} x \; \exp(-x^2), \quad (40)$$

$$G_\gamma = -\frac{2\pi |G_{mn}|^2}{3(\Gamma_m + \gamma_m) k\overline{v_1}}\left[\frac{2}{3}\left(\frac{13}{5}\pi^{3/2} - 1\right)x - \frac{2\pi^{3/2} - 1}{3} \; x^3 + \ldots\right]. \quad (41)$$

The contribution of the third term in parentheses in Eq. (31) for G_γ, containing $\overline{\kappa_2}$, is less than 5%. Now we neglect this term and obtain instead of Eq. (41) the following formula:

$$G_\gamma = -\frac{4\pi^{3/2}|G_{mn}|^2}{15(\Gamma_m+\gamma_m)k\overline{v_1}}(13+8x^2)x\ \ \exp(-x^2). \tag{42}$$

Coefficient G_d can be written as

$$G_d = -\frac{2\pi^{1/2}|G_{mn}|^2}{(\Gamma_m+\gamma_m)k\overline{v_1}}\left[\frac{2\pi}{15}A\ (13+8x^2) - G_u\ \frac{2n_2 d_n/d_{n2}}{n_2+(m_1/m_2)^{3/2}n_1}\right]x\ \ \exp(-x^2). \tag{43}$$

In the case of homogeneous broadening ($y \gg 1$) for $|x| \ll y$ we obtain

$$G_s = -\frac{2\pi^{1/2}|G_{mn}|^2}{3(\Gamma_m+\gamma_m)\Gamma}\ \frac{x}{y^2}, \tag{44}$$

$$G_\gamma = -\frac{2|G_{mn}|^2}{3\pi^{1/2}(\Gamma_m+\gamma_m)\Gamma}(10\pi^{3/2}-4)\ \frac{x}{y^2},$$

$$G_d = -\frac{2|G_{mn}|^2}{(\Gamma_m+\gamma_m)\Gamma}\left[A\ \frac{10\pi^{3/2}-4}{3\pi^{1/2}} - G_u\ \frac{2n_2 d_n/d_{n2}}{n_2+(m_1/m_2)^{3/2}n_1}\right]\frac{x}{y^2}.$$

V. DISCUSSION

The kinetic coefficients G_s and G_d characterizing the surface and bulk mechanisms of photophoresis are proportional to the radiation intensity. They depend on the frequencies' ratio Γ_m/Γ_m, the magnitude of the detuning Ω, composition of the gaseous mixture, and masses and diameters of the molecules.

The values of the modified kinetic coefficients G_s and G_d as functions of the detuning parameter $x=\Omega/k\overline{v_1}$ for various values of the broadening parameter $y=\Gamma/k\overline{v_1}$ are shown in Figs. 2 and 3. Using the preceding notation we take

$$G_s^* = \left(\frac{8|G_{mn}|^2}{(\Gamma_m+\gamma_m)k\overline{v_1}}\right)^{-1}G_s,$$

$$G_d^* = \left(\frac{4|G_{mn}|^2}{(\Gamma_m+\gamma_m)k\overline{v_1}}\right)^{-1}G_d.$$

Direction of the force and velocity of photophoresis depends on the sign of the detuning Ω, i.e., the kinetic coefficients G_s and G_d and hence μ_s and μ_d are odd functions of Ω (Figs. 2 and 3). In the case of inhomogeneous broadening, the photophoretic velocity peaks at $\Omega \approx k\overline{v_1}$. When $|\Omega| \geq 3k\overline{v_1}$, the effect is negligible because it does not satisfy the resonance condition.

The kinetic coefficients G_s and G_d are positive if the detuning parameter $x=\Omega/k\overline{v_1}$ is negative. At $x>0$ both G_s and G_d are negative.

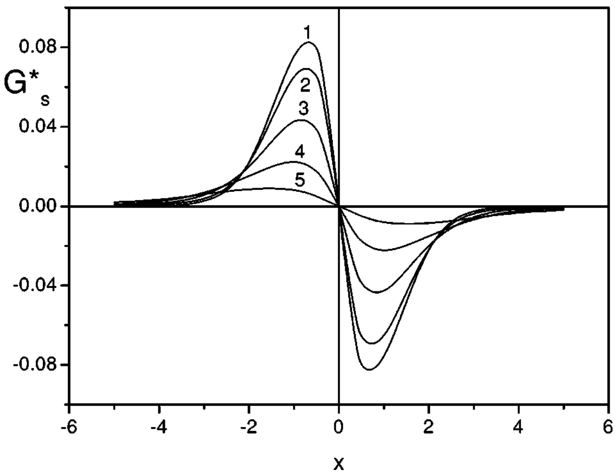

FIG. 2. G_s^* as a function of the detuning parameter x at various values of broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5) at $n_1 \approx n_2$, $m_1 \approx m_2$, and $d_n \approx d_2$.

Thus, the directions of the surface components of the force and velocity of photophoresis are determined by the signs in the difference of the accommodation coefficients for the unexcited and excited molecules, $\Delta\varepsilon = \varepsilon_n - \varepsilon_m$, and the frequency detuning Ω. In the case when $\Delta\varepsilon>0$, the direction of the surface component coincides with the direction of light propagation at $\Omega<0$, and it is opposite to the direction of light propagation at $\Omega>0$.

To account for this result, we examine the special case when the ground-state molecules have bigger accommodation coefficient, $\Delta\varepsilon>0$, and the frequency detuning is positive, $\Omega>0$. In this case the flow of excited molecules is aligned with the wave vector $(u_m>0)$, while the direction of the flow of ground-state molecules is opposite, $(u_n<0)$. Hence, when $\varepsilon_n>\varepsilon_m$, the flux of the ground-state molecules experiences greater drag when flowing around the aerosol particle than the flux of the excited molecules. Thus the re-

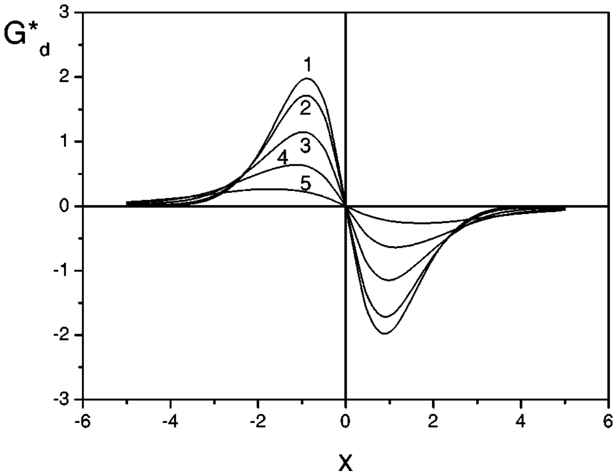

FIG. 3. G_d^* as a function of the detuning parameter x at various values of broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5) at $n_1 \approx n_2$, $m_1 \approx m_2$, and $d_n \approx d_2$.

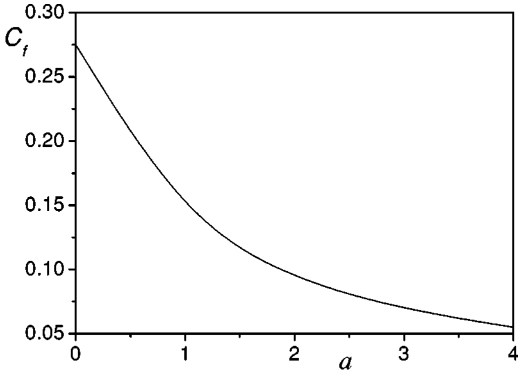

FIG. 4. Photophoretic velocity as a function of the concentration parameter $a=n_2/n_1$ for $x=0.75$, $m_1=m_2$, $\gamma_m \ll \Gamma_m$, $d_n=d_2$, $\varepsilon_n=\varepsilon_2=1$, and $\Delta\varepsilon=\Delta d/d_n=-0.1$.

sultant force acts upon the particle along the direction of the flux of ground-state molecules, i.e., in opposite direction to the light propagation.

The directions of the bulk components of the force and velocity of the photophoresis are determined by the difference of the effective diameters of molecules in the ground-state and excited state, $\Delta d=d_n-d_m$, and by the frequency detuning Ω. In the case when $\Delta d>0$, the bulk component of the force is aligned with the direction of the light propagation at $\Omega<0$ and it is opposed to the direction of the light propagation at $\Omega>0$.

It can be explained as follows. We assume that Ω is positive. We also suppose that the effective diameter of molecules that have absorbed light increases $(\Delta d<0)$. Therefore the mean free path of these molecules decreases. Then the flux of excited molecules, moving in the direction of the wave vector, experiences a greater drag when flowing around the particle than the flux of ground-state molecules. Thus, the gas acts upon the aerosol particle in the direction of light propagation.

Consider the dependence of the force F_R and velocity U_f of photophoresis on the concentration parameter $a=n_2/n_1$ and the ratio of molecular masses $b=m_1/m_2$. The results of numerical calculations of the velocity U_f depending on the concentration parameter a are shown in Fig. 4. Under the condition of fixed number density of the mixture $(n=n_1+n_2=\text{const})$, growth of the concentration of the buffer gas leads to the decrease of U_f.

Combining Eqs. (38) and (39), one can obtain an approximate expression for the photophoretic velocity at a given pressure of the gas mixture,

$$C_f=\frac{U_f(a)}{\overline{v_1}}\approx\frac{U_f(a=0)}{\overline{v_1}(1+b^{-1/2}a)}, \tag{45}$$

where $U_f(a=0)$ is the photophoretic velocity in the absence of a buffer gas. Note that Eq. (45) provides a satisfactory approximation to the results of numerical calculations.

The dependence of the photophoretic velocity on the ratio of molecular masses of the absorbing and buffer gases, $b=m_1/m_2$, is shown in Fig. 5. As may be seen from this figure, the particle velocity increases monotonically with b for $b\leqslant 20$. In the case where the molecule of absorbing gas is much easier than the molecule of the buffer gas $(m_1 \ll m_2)$ the photophoretic velocity is proportional to $\sqrt{m_1/m_2}$. On the other hand, for a heavy absorbing gas $(m_1 \gg m_2)$ the photophoretic velocity is independent of b, and it is equal to the particle velocity in a pure absorbing gas.

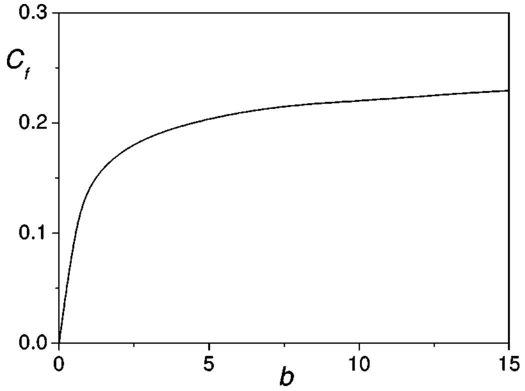

FIG. 5. Dependence of photophoretic velocity on the ratio of molecular masses $b=m_1/m_2$ for $x=0.75$, $n_1=n_2$, $\gamma_m \ll \Gamma_m$, $d_n=d_2$, $\varepsilon_n=\varepsilon_2=1$, and $\Delta\varepsilon=\Delta d/d_n=-0.1$.

Now we perform numerical estimations for a specific system under typical experimental conditions. We consider an aluminum particle of radius $r_0=1\ \mu$m placed (1) in the sodium vapor and (2) in the equimolar mixture of the sodium vapor and argon. The temperature is $T_0=700$ K. The saturated vapor pressure for sodium at this temperature is 306 Pa [11].

The molecular characteristics of Na and Ar are

$$m_1=3.82\cdot 10^{-26}\ \text{kg},\quad m_2=6.64\cdot 10^{-26}\ \text{kg},$$

$$d_1=3.0\ \text{Å},\quad d_2=3.4\ \text{Å}.$$

The source of light is a tunable dye laser emitting in the vicinity of the D_1 and D_2 lines of sodium (wavelength $\lambda_0 \approx 600$ nm).

In this case the frequency of the incident light turns out to be much bigger than the electron collision rate in the metal, and it much smaller than the plasma frequency. Langmuir screening [12] takes place, i.e., light is reflected by the particle with no absorption. Hence, under these conditions the model of a nonabsorbing particle usually adopted in theory is valid.

Consider the radiated power of ~10 mW and the beam diameter of ~1 mm. At this intensity the Rabi frequency G_{mn} [see Eq. (5)] is about 10^8 Hz. The radiative decay rate is $\Gamma_m \approx 6\cdot 10^7$ Hz [13]. Finally, the Doppler broadening, $k\overline{v_1}\approx 7.3\times 10^9$ Hz, corresponds to inhomogeneous broadening of the absorption line, $y=\Gamma/k\overline{v_1}\approx 0.01$.

Consider the following two different cases.

a. Pure gas $(n_2=0)$. In this case the collision rate of the excited molecules and the Knudsen number are $\gamma_m \approx 7.1\times 10^6$ Hz and $Kn \approx 100$, respectively, which that corresponds to the free-molecular regime.

Numerical estimates of the kinetic coefficients yield

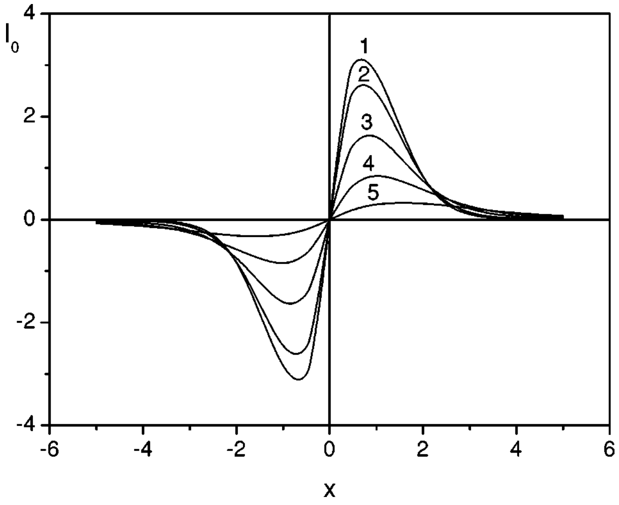

FIG. 6. I_0 as a function of the detuning parameter x at various values of broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

$$G_s=-0.042x\ \exp(-x^2),$$

$$G_d=-0.030(13+8x^2)x\ \exp(-x^2).$$

Assuming $x=\Omega/k\overline{v_1}=0.8$ and $\Delta\varepsilon=\Delta d/d_n=-0.01$, we get the following values of the kinetic coefficients: $G_s=-0.016$ and $G_d=-0.228$. For the photophoretic force we obtain $F_R=9.3\times10^{-11}$ N. It is important to note that the gravitational force acting upon the particle is 1.1×10^{-14} N, which ~0.01% of the photophoretic force.

Assuming $\varepsilon_n=1$, one calculates particle velocity $U_f=0.03\overline{v_1}=20\ \mathrm{ms}^{-1}$, that is, ~6% of the sound speed.

b. Equimolar mixture $Na+Ar(n_1=n_2)$. The numerical values of the input parameters are the same as those in the preceding case. Equation (38) yields the estimation of the particle velocity, $U_f=7\ \mathrm{ms}^{-1}$.

ACKNOWLEDGMENTS

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APPENDIX A

The expressions for the rates $\nu_{ij}^{(k)}$ that enter Eq. (14) have the form [7]

$$\nu_{ij}^{(1)}=\frac{16}{3}\ \frac{m_{ij}}{m_i}\ n_j\Omega_{ij}^{(1,1)}\ ,\qquad m_{ij}=\frac{m_i m_j}{m_i+m_j},$$

$$\nu_{ij}^{(2)}=\frac{64}{15}\left(\frac{m_{ij}}{m_i}\right)^2 n_j\left(\Omega_{ij}^{(1,2)}-\frac{5}{2}\ \Omega_{ij}^{(1,1)}\right),$$

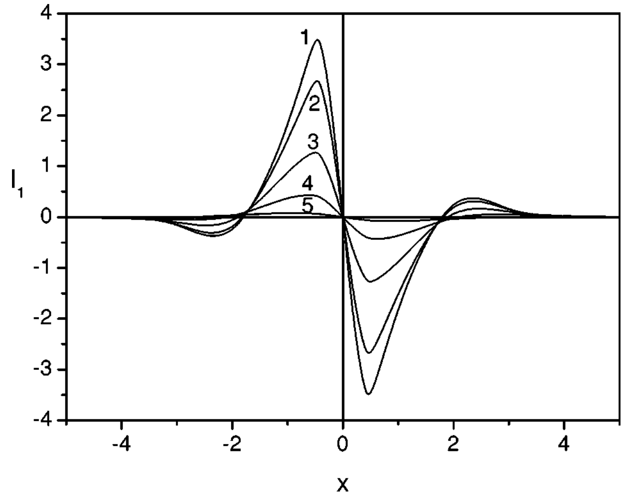

FIG. 7. I_1 as a function of the detuning parameter x at various values of broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

$$\nu_{ij}^{(5)}=\frac{64}{15}\left(\frac{m_{ij}}{m_i}\right)^3\frac{m_i}{m_j}\ n_j\Bigg[\Omega_{ij}^{(2,2)}+\left(\frac{15}{4}\ \frac{m_i}{m_j}+\frac{25}{8}\ \frac{m_j}{m_i}\right)\Omega_{ij}^{(1,1)} -\frac{1}{2}\ \frac{m_j}{m_i}(5\Omega_{ij}^{(1,2)}-\Omega_{ij}^{(1,3)})\Bigg],$$

$$\nu_{ij}^{(6)}=\frac{64}{15}\left(\frac{m_{ij}}{m_i}\right)^3\left(\frac{m_i}{m_j}\right)^{3/2} n_j\Bigg[-\Omega_{ij}^{(2,2)}+\frac{55}{8}\ \Omega_{ij}^{(1,1)} -\frac{5}{2}\ \Omega_{ij}^{(1,2)}+\frac{1}{2}\ \Omega_{ij}^{(1,3)}\Bigg].$$

Here $\Omega_{ij}^{(l,r)}$ are the Chapman-Cowling integrals [14].

APPENDIX B

Here we find the dependence of κ_0, κ_1. and, $\overline{\kappa_2}$ on the parameters $x=\Omega/(k\overline{v_1})$ and $y=\Gamma/(k\overline{v_1})$. It is convenient to write

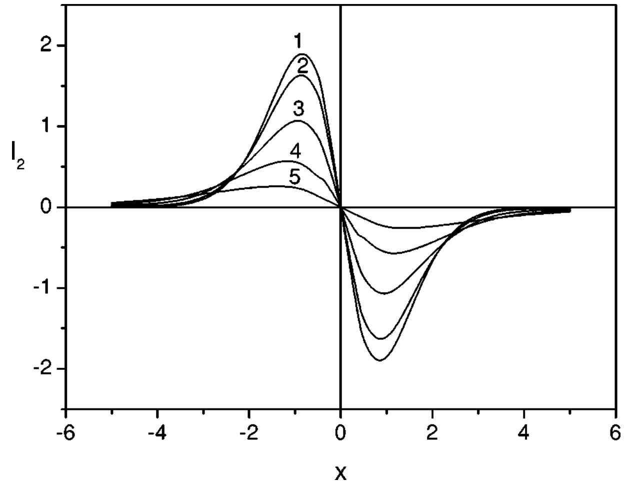

FIG. 8. I_2 as a function of the detuning parameter x at various values of broadening parameter $y=0.1$ (curve 1), 0.2 (curve 2), 0.5 (curve 3), 1 (curve 4), and 2 (curve 5).

$$\kappa_0=\frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1}\,I_0(x,y),\quad \kappa_1=\frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1}\,I_1(x,y),$$

$$\overline{\kappa_2}=\frac{4G_{mn}^2}{\Gamma_m k\overline{v}_1}\;I_2(x,y).$$

For inhomogeneous broadening ($y \ll 1$) we obtain

$$I_0=\pi^2 x\;\;\exp(-x^2),\quad I_2=\frac{\pi^{3/2}}{3}(-2x+x^3+\cdots),$$

$$I_1=\pi^2\left(x^2-\frac{3}{2}\right)x\;\;\exp(-x^2).$$

For homogeneous broadening ($y \gg 1$) with $x<y$ we have, to within terms of the order of x/y,

$$I_0=\pi^{3/2}\,\frac{x}{y^3},\quad I_1=0,\quad I_2=-\frac{4\pi}{3}\,\frac{x}{y^3}.$$

The results of numerical calculation for various values of the parameters x and y are plotted in Figs. 6–8.

[1] S.A. Beresnev, V.G. Chernyak, and G.A. Fomyagin, Phys. Fluids A **5**, 2043 (1993).

[2] F.Kh. Gel'mukhanov, and A.M. Shalagin, JETP Lett. **29**, 711 (1979).

[3] B.V. Derjaguin, and V.I. Roldughin, J. Colloid Interface Sci. **122**, 537 (1988).

[4] V.G. Chernyak, Zh. Éksp. Teor. Fiz. **96**, 878 (1989) [Sov. Phys. JETP **69**, 498 (1989)].

[5] H. Grad, Commun. Pure Appl. Math. **2**, 331 (1949).

[6] F.Kh. Gel'mukhanov, and L.V. Il'ichev, Khim. Fiz. **3**, 1544 (1984).

[7] F.J. McCormack, Phys. Fluids **16**, 2095 (1973).

[8] S.J. van Enk and G. Nienhuis, Phys. Rev. A **41**, 3757 (1990).

[9] V.G. Chernyak and O.V. Klitenik, Phys. Rev. E **65**, 036125 (2002).

[10] L. Waldmann, Z. Naturforsch. A **14**, 589 (1983).

[11] N.B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases: In Normal and Dissociated States*, 2nd ed. (Halsted Press, New York, 1975).

[12] E.A. Turov, *Constitutive Equations of Electrodynamics* (in Russian) (Nauka, Moskow, 1983).

[13] A.A. Radtsig and B.M. Smirnov, *Reference Data on Atoms, Molecules, and Ions* (Springer-Verlag, Berlin, 1985).

[14] S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, London, 1952).