Photophoresis in selectively excited gas

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The motion of an aerosol particle due to resonant optical radiation is studied. Radiation is absorbed velocity-selectively by molecules of one of the components of a gaseous mixture. Equations are derived for photophoretic force and velocity in the free molecule regime. The dependence of these characteristics on detuning the radiation frequency from an absorption line center and on accommodation and transport characteristics of exited and unexcited molecules is analyzed.

Radiometric photophoresis[1] is caused by inhomogeneous heating of an absorbing aerosol particle, i.e., this is the case that radiation interacts with a particle and does not interact with gas.

It is of interest to study the motion of aerosol particles in the field of optical radiation, whose frequency is close to the frequency of quantum transitions in a gas molecule. In this case the radiation is absorbed by gas.

Due to the Doppler effect the radiation is absorbed selectively with respect to molecular velocities. As this takes place, light-induced flows of matter and energy arise in the gas.[2] Different scattering of excited and unexcited molecules at a particle surface and their different transport interaction cross sections lead to appearance of a resonant photophoretic force acting on a particle.[3,4]

Photophoresis of a particle in a one-component gas was considered in Refs. 3 and 4. In Ref. 3, the Grad 13-moment approximation[5] is used, in which the distribution function is approximated through a finite number of its moments. Thus, the distribution functions of excited and unexcited molecules depend on the spatially averaged velocities and ignore significant peculiarities in a narrow velocity range, which is determined by the condition of selective light absorption.[2] Reference 4 considered only the accommodation mechanism of the photophoresis, which arises due to different coefficients of pulse accommodation in excited and unexcited gas molecules. The volume mechanism caused by different transport characteristics of molecules in the ground and excited states was beyond the scope of Ref. 4.

If an aerosol particle is suspended in a mixture of absorbing and buffer gases, then we can predict an additional factor determining the photophoresis magnitude. The total momentum transferred to a particle turns out to be uncompensated due to, besides other factors, the different masses of molecules in the gas mixture, in which the macroscopic flows of the absorbing and buffer gases are of opposite directions.[2] It is also obvious that the photophoretic force depends on the concentration of gas mixture components.

In this paper, we consider photophoresis of an non-absorbing (or homogeneously absorbing) particle suspended in a two-component gas mixture, in which absorbing gas molecules are velocity-selectively excited by the resonance optical radiation. The free molecule regime is considered, in which the molecules' mean free path far exceeds the particle size.

1. Formulation of the problem

Consider a spherical aerosol particle of radius r_0 suspended in a two-component gas mixture. The system is in the thermodynamic equilibrium at the temperature T_0.

Let the system be exposed to monochromatic traveling-wave radiation directed along the axis Z (Fig. 1).

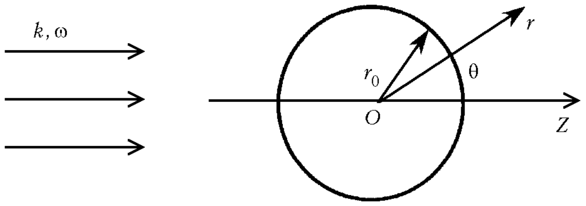

Fig. 1. Problem geometry.

The radiation is absorbed by molecules of one component at an electronic or rotational-vibrational transition from the ground state n to the first excited state m. The radiation frequency ω is slightly detuned from the absorption line center ω_{mn}, that is, $\Omega = \omega - \omega_{mn}$ ($|\Omega| \ll \omega, \omega_{mn}$).

Because of the Doppler effect, the radiation is absorbed velocity-selectively by those molecules, whose velocity projection v_z onto the radiation direction is close to the resonance value $v_{\text{res}} = \Omega/k$, where k is the value of the wave vector $\mathbf{k}$. The effective interval $\Delta\mathbf{v}$ of resonance velocities is determined by the condition $\mathbf{k}\Delta\mathbf{v} \sim \Gamma$, where Γ is the homogeneous halfwidth of the absorption line. The molecules absorbing the radiation excite. The resulting velocity distribution of unexcited molecules of the absorbing gas has a Bennett dip at the interval $\Delta\mathbf{v}$, and the corresponding fraction of excited molecules form the Bennett peak.[6] The position of the Bennett peak and dip is determined by the sign and value of detuning Ω of the radiation frequency from the absorption line center.

If the excited and unexcited molecules differently interact with the aerosol particle surface and with buffer gas molecules, then the rates of destruction of the Bennett peak and smoothing of the Bennett dip are different. As the result, the total velocity distribution of active gas molecules differs from the Maxwell one. A well-known consequence of this at $\Omega \neq 0$ is the light-induced drift of the absorbing gas.[2] Macroscopic flows collinear to the wave vector $\mathbf{k}$ arise in the gas mixture. These flows consisting of excited and unexcited molecules of the absorbing gas and the buffer gas undergo different resistance when flowing around a particle because of the excited and unexcited molecules of the absorbing gas, as well as molecules of the buffer gas differently interact with the particle surface and have different transport characteristics and masses. Thus, the gas transfers the uncompensated momentum to the particle, that is, a force parallel to the axis Z acts upon the particle.

Indices 1 and 2 denote the characteristics of the absorbing and buffer gases, respectively, and indices m and n denote characteristics of excited and unexcited molecules. The absorbing gas consists of molecules having the same mass m_1 and different effective diameters $d_n \neq d_m$.

If the velocity distributions of the excited f_m, unexcited f_n, and buffer gas f_2 molecules are known, then the photophoretic force can be calculated as

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

It is well-known[6,7] that in the two-level approximation for the absorbing molecules the velocity distributions f_n, f_m, and f_2 meet the system of the following kinetic equations:

$$\frac{\partial f_m}{\partial t} + \mathbf{v}\nabla f_m = \frac{1}{2}\chi(\mathbf{v})\Gamma_m (f_n - f_m) - \Gamma_m f_m + S_m \,, \qquad (2)$$

$$\frac{\partial f_n}{\partial t} + \mathbf{v}\nabla f_n = -\frac{1}{2}\chi(\mathbf{v})\, \Gamma_m (f_n - f_m) + \Gamma_m f_m + S_n \,, \qquad (3)$$

$$\frac{\partial f_2}{\partial t} + \mathbf{v}\nabla f_2 = S_2 \,, \qquad (4)$$

where

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

$$\chi(\mathbf{v}) = \frac{4}{\Gamma_m} G^2 \frac{\Gamma}{\Gamma^2 + (\Omega - kv)^2}\,; \quad G = \left| \frac{d_{mn} E_0}{2\hbar} \right|; \qquad (5)$$

Γ_m is the frequency of radiative decay of the excited level; $\chi(\mathbf{v})$ determines the absorption probability per unit time for molecules with the given velocity $\mathbf{v}$; d_{mn} is the matrix element of the $m - n$ transition dipole moment; E_0 is the amplitude of the electric field of the light wave; S_{ij} are the Boltzmann integrals of collisions between molecules of the ith and jth kinds; $\hbar$ is the Planck's constant.

As boundary conditions for Eqs. (2)–(4), we have to specify the distribution functions $f_i^+(\mathbf{r}_0, \mathbf{v})$ $(i = m, n, 2)$ for molecules emitted from the particle surface. In the general case, the surface temperature differs from the equilibrium temperature T_0. This can be connected with radiation absorption by the particle. The particle is assumed either absorbing or non-absorbing, but having the homogeneous temperature. Radiometric photophoresis does not occur in this case. Therefore, we assume the particle temperature equal to the temperature of the gas mixture.

Let the fraction ε_i of molecules of the ith kind be reflected diffusely by the particle surface with the Maxwell distribution f_i^s corresponding to the temperature T_0 and the density n_{is}, and the fraction $(1 - \varepsilon_i)$ be reflected specularly. Then, neglecting quenching or excitation of molecules at a collision with the surface, for molecules of the ith kind we have:

$$f_i^+(r_0, v) = \varepsilon_i f_i^s + (1 - \varepsilon_i) f_i^- [\mathbf{v} - 2(\mathbf{vn})],$$
$$i = m,\, n,\, 2;\ (\mathbf{vn}) > 0, \qquad (6)$$

$$f_i^s = n_{is} \left(\frac{m_i}{2\pi k_B T_0} \right)^{3/2} \exp\left(-\frac{v^2}{\bar{v}_i^2} \right), \quad \bar{v}_i = \left(\frac{2 k_B T_0}{m_i} \right)^{1/2},$$

where $\mathbf{n} = \mathbf{r}_0 / r_0$ is the external normal to the particle surface; $f_i^-(\mathbf{v})$ is the distribution function of the molecules colliding with the surface; m_i is the mass of a molecule of the ith kind; k_B is the Boltzmann constant.

In Eq. (6) the unknown densities n_{is} of molecules reflected from the aerosol particle surface can be found from no-pass conditions.

The distribution f_i^- of molecules colliding with the particle is to be determined from solution of the kinetic equations (2)–(4).

Let us restrict our consideration to analysis of the free molecule regime, when the molecule mean free path is much larger than the particle radius. In this case we can neglect the fact that the distribution of molecules colliding with the particle is disturbed due to collisions with emitted molecules.

Assume that the cross dimension of the light ray is much larger than the particle radius and the molecule mean free path. Then the radiation intensity can be thought independent of coordinates, so the distributions formed due to collisions between molecules, that is, far from the particle, are spatially homogeneous. In this case, we can neglect the coordinate derivatives in Eqs. (2)–(4), the distribution functions f_i^- of molecules colliding with particle meet to.

Let the radiation be continuous and the gas state be stationary. Then the time derivatives in Eqs. (2)–(4) disappear.

Consider the case of small, on the average, value of $\chi(\mathbf{v})$, that is usually fulfilled for rotational-vibrational transitions. For electronic transitions this condition is fulfilled only at low radiation intensity.

With allowance for the above assumptions, Eqs. (2)–(4) and boundary conditions (6) can be linearized.

Then consider molecules as solid elastic spheres with the effective diameters d_i $(i = m, n, 2)$ and use the approximating collision integrals.[8] Besides, take into account the experimentally established fact of small difference between the diameters of excited and unexcited molecules, that is, $|d_n - d_m|/d_n \ll 1$.

Thus, Eqs. (2)–(6) completely determine the distribution functions of molecules colliding with the particle and reflected from it.

2. Photophoretic force and velocity

Using the obtained distribution functions and Eq. (1), we obtain the following equation for the photophoretic force:

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

$$\Delta\varepsilon = \varepsilon_n - \varepsilon_m,\ \Delta d = d_n - d_m. \qquad (7)$$

Here $p_1 = n_1 k_\mathrm{B} T_0$ is the partial pressure of the absorbing gas.

The kinetic coefficient G_ε characterizes the surface mechanism of photophoresis due to the different coefficients of specular and diffuse reflection of excited and unexcited molecules. The coefficient G_d characterizes the volume mechanism of photophoresis connected with the different transport properties of excited and unexcited molecules.

In the general case, the obtained equations for the kinetic coefficients G_ε and G_d have a cumbersome form. If we restrict our consideration to inhomogeneous broadening of a spectral line that is typical of rarefied gases $(\Gamma \ll k\,\bar{v}_1)$, then these equations can be considerably simplified:

$$G_\varepsilon = -\frac{2\pi G^2}{3(\Gamma_m + \gamma_m)k\bar{v}_1} x \exp\left(-x^2\right), \qquad (8)$$

$$G_d = -\frac{2\pi^{1/2} G^2}{(\Gamma_m + \gamma_m)k\bar{v}_1} \times$$

$$\times\left[A\frac{2\pi}{15}(13 + 8x^2) - B\frac{2n_2\, d_n/d_{n2}}{n_2 + (m_1/m_2)^{3/2} n_1}\right] x \exp\left(-x^2\right),$$

where

$$A = \frac{\sqrt{m_1/2}\, n_1 d_n^2 + \sqrt{m_{12}}\, n_2 d_n d_{n2}}{\sqrt{m_1/2}\, n_1 d_n^2 + \sqrt{m_{12}}\, n_2 d_{n2}^2},\ \ d_{n2} = \frac{1}{2}(d_n + d_2),$$

$$m_{12} = \frac{m_1 m_2}{m_1 + m_2};$$

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

$$x = \frac{\Omega}{k\bar{v}_1};$$

γ_m is the effective frequency of collisions of excited molecules.

Under the effect of the photophoretic force F_R, the particle is accelerated until the absolute value of the resistance force of the gas mixture F_c becomes equal to F_R. From the condition $|F_c| = F_R$ we can find the established velocity U_f of the aerosol particle.

The resistance force in the free molecule regime with allowance for the low concentration of excited molecules $(n_m \ll n_n)$ can be found as[9]:

$$F_c = -\frac{8\pi^{1/2}}{3} r_0^2 m_1 n_1 \bar{v}_1 \alpha U_\mathrm{f},$$

$$\alpha = 1 + \varepsilon_n \frac{\pi}{8} + \frac{n_2}{n_1}\left(\frac{m_2}{m_1}\right)^{1/2}\left(1 + \varepsilon_2 \frac{\pi}{8}\right). \qquad (9)$$

Thus, the established velocity of the particle motion relative to the center of gravity of the gas mixture is

$$U_\mathrm{f} = \bar{v}_1\left(\mu_\varepsilon \Delta\varepsilon + \mu_d \frac{\Delta d}{d_n}\right);$$

$$\mu_\varepsilon = \frac{3\pi^{1/2}}{4\alpha} G_\varepsilon,\ \ \mu_d = \frac{3\pi^{1/2}}{4\alpha} G_d, \qquad (10)$$

where μ_ε and μ_d are the kinetic coefficients characterizing, respectively, the surface and the volume mechanisms of photophoretic velocity.

3. Discussion

The kinetic coefficients G_ε and G_d depend on the ratio between the frequencies of the radiative decay of the excited level Γ_m and collisions between molecules γ_m, detuning Ω of the radiation frequency from the absorption line center, component concentrations, and molecular mass ratios.

Figure 2 illustrates the dependence of the modified kinetic coefficients on the parameters of detuning $x = \Omega/k\,\bar{v}_1$ and broadening $y = \Gamma/k\,\bar{v}_1$:

$$G_\varepsilon^* = \left(\frac{8G^2}{k\bar{v}_1(\Gamma_m + \gamma_m)}\right)^{-1} G_\varepsilon,$$

$$G_d^* = \left(\frac{4G^2}{k\bar{v}_1(\Gamma_m+\gamma_m)}\right)^{-1} G_d .$$

The direction of the photophoretic force and velocity depends on the sign of detuning Ω, because the kinetic coefficients G_ε and G_d and, consequently, μ_ε and μ_d are odd functions of Ω (Fig. 2). The photophoretic velocity is maximal at $\Omega \approx k\,\bar{v}_1$. At $|\Omega| > 3k\,\bar{v}_1$ the effect is negligibly small, because the resonance condition breaks and only a small part of molecules excite through radiation absorption.

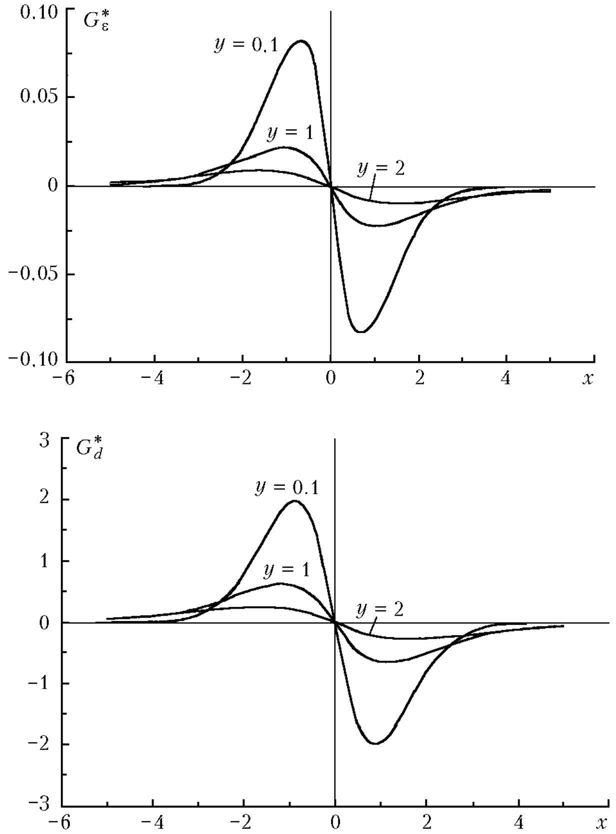

Fig. 2. Dependence of the kinetic coefficients $G_\varepsilon^*(x, y)$ and $G_d^*(x, y)$ on the detuning x and broadening y.

The direction of the surface component of the photophoretic force and velocity is determined by signs of the difference between the specular and diffuse reflection coefficients of excited and unexcited molecules $\Delta\varepsilon$ and detuning Ω. If $\Delta\varepsilon > 0$, then the direction of the surface component at $\Omega < 0$ coincides with the radiation direction, and at $\Omega > 0$ it has the opposing direction.

The direction of the volume component of the photophoretic force and velocity is determined by the signs of the difference between the effective diameters of excited and unexcited molecules Δd and detuning Ω. If $\Delta d > 0$ then the direction of the volume component at $\Omega < 0$ coincides with the radiation direction, and at $\Omega > 0$ it is opposing.

Let us present some estimates for typical experimental conditions. Consider an aluminum particle with the radius $r_0 = 1$ μm in the sodium vapor and in the equimolar mixture of the sodium vapor with argon at the temperature $T_0 = 700$ K. The saturated vapor pressure is 306 Pa (Ref. 10).

Molecular characteristic of Na and Ar are the following:

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

$$d_1 = 3\ \text{Å},\ d_2 = 3.4\ \text{Å};\ \bar{v}_1 \approx 711\ \text{m/s}.$$

A tunable dye laser with the frequency nearby D_1 and D_2 sodium lines is a radiation source (wavelength $\lambda = 600$ nm).

In this case, the frequency of the incident radiation proves to be much higher than the frequency of electron collisions in metal and lower than the plasma frequency. Therefore, Langmuir screening takes place,[11] that is, the radiation energy is reflected by the particle almost without absorption. Consequently, the theoretically accepted model of a non-absorbing particle is realized under these conditions.

Let the radiation power be 10 mW, the ray diameter be 1 mm (radiation intensity $I \approx 1$ W/cm^2). Then the Rabi frequency $G \approx 10^8$ Hz. The frequency of radiative decay $\Gamma_m = 6 \cdot 10^7$ Hz (Ref. 12). The Doppler broadening $k\,\bar{v}_1 \approx 7.3 \cdot 10^9$ Hz, that corresponds to the inhomogeneous broadening of the spectral line, $\Gamma/(k\,\bar{v}_1) \approx 0.01$.

1. Pure gas ($n_2 = 0$).

In this case, the collision frequency of excited molecules and the Knudsen number are $\gamma_m \approx 7.1 \cdot 10^6$ Hz and Kn ≈ 100, that corresponds to the free molecule regime.

Let $x = \Omega/k\bar{v}_1 = 0.8$ and $\Delta\varepsilon = \Delta d/d_n = -\,0.1$. These parameters obtained from experimental investigations of light-induced drift in capillaries range within 0.01–0.1 (Refs. 13 and 14). Then for the photophoretic force we have $F_R \approx 9.3 \cdot 10^{-11}$ N. Note that the force of gravity acting on the particle $Mg \approx 1.1 \cdot 10^{-14}$ N makes up about 0.01% of the photophoretic force.

Estimate now the velocity acquired by the particle. Let $\varepsilon_n = 1$, then $U_\text{f} \approx 0.03\,\bar{v}_1 \approx 20$ m/s, that is, about 6% of the sonic speed.

2. Equimolar mixture Na + Ar ($n_1 = n_2$).

The parameters have the same values as in the previous case. Then the particle velocity can be estimated as $U_\text{f} \approx 7$ m/s.

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