PHOTOPHORETIC MOTION OF A SMALL VOLATILE PARTICLE IN A MOLECULAR GAS

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Photophoresis of a small volatile particle in a molecular gas is examined. Expressions are obtained for the surface temperature, force on, and velocity of the particle. The effect of volatility on the characteristics of the motion is discussed.

The motion of a solid spherical particle in a simple gas in an optical radiation field in the free molecular regime was studied in [1-3]. In this case, it was assumed that the particle absorbs all radiation incident on it. A rigorous calculation of the heat absorbed by the particle is possible based on Mie's theory [4]. This approach was first used in [5], but the expression for the photophoretic force was not obtained with a rigorous method. Later the paper [6] appeared in which this deficiency was corrected, but nevertheless certain inaccuracies in determining the temperature field inside the particle remained.

In the present paper, the problem is extended to the case of a moving volatile particle in a molecular gas.

Let us consider a spherical particle with radius R, located in its own vapor, whose molecules have internal degrees of freedom. It is irradiated from one side along the OZ axis by a plane unpolarized wave of monochromatic light with wavelength λ and intensity $\vec{I}$. We assume that $R \ll \lambda$ and that the average mean free path length of molecules is $l \gg R$. These conditions are satisfied in the earth's atmosphere by submicron particles. The origin of the system of coordinates is placed at the center of the particle. The temperature and number density of the vapor in the unperturbed region are T_∞ and n'_∞. The relative oversaturation is defined by the quantity $\nu_\infty = (n'_\infty - n_\infty)/n_\infty$, where n_∞ is the density of the saturated vapor at temperature T_∞. The distribution function of molecules incident on the particle in the i-th internal state corresponds to the function far away from the particle and after linearization has the form [7]

$$f_i^- = f_{\infty i}\left[1 + \nu_\infty + 2c_z u_\infty\right], \tag{1}$$

where

$$f_{\infty i} = n_\infty \left(\frac{m}{2\pi k T_\infty}\right)^{3/2} \frac{\exp(-c^2 - \varepsilon_i)}{\sum\limits_i \exp(-\varepsilon_i)}; \quad \varepsilon_i = \frac{E_i}{kT_\infty}; \quad \vec{c} = \sqrt{\frac{m}{2kT_\infty}}\,\vec{v};$$

$\vec{u}_\infty$ is the dimensionless (in units of $\sqrt{2kT_\infty/m}$) velocity of the unperturbed vapor flux.

It is assumed that out of the total number of molecules emitted by a surface element, the fraction α_m is evaporated at equilibrium with the local value of the surface temperature T_s and the fraction $(1 - \alpha_m)$, which does not condense when colliding with the particle, is reflected:

$$f_i^+ = \alpha_m f_{si} + (1 - \alpha_m) f_{ri}. \tag{2}$$

Assume that the quantity $T_s(\theta)$ differs insignificantly from T_∞, i.e.,

$$T_s(\theta) = T_\infty\left[1 + \tau_s(\theta)\right]; \quad |\tau_s| \ll 1,$$

where θ is the polar angle measured from the positive OZ axis in a counterclockwise direction.

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The density of the saturated vapor near the particle surface taking into account its curvature equals

$$n_s' = n_s \exp\left(\frac{2\sigma^* V_p}{RkT_s}\right) \simeq n_\infty \exp(\gamma)\,[1+\nu_s-\gamma\tau_s],$$

where $n_s(\theta) = n_\infty\,[1 + \nu_s(\theta)]$ is the density of the saturated vapor above a flat surface at temperature T_s; $\gamma = 2\sigma^* V_p/RkT_\infty$; and σ^* is the surface tension.

The quantities τ_s and ν_s are related by the linearized Clapeyron–Clausius equation:

$$\nu_s(\theta) = (\beta-1)\,\tau_s(\theta), \quad \beta = \frac{L}{kT_\infty},$$

where L is the latent heat of vaporization (condensation) per molecule in the vapor. Then, the distribution function of the evaporated molecules has the form

$$f_{si} = f_{\infty i} \exp(\gamma)\left[1 + \left(c^2 - \frac{5}{2} + \beta - \gamma + \varepsilon_i - \langle\varepsilon\rangle\right)\tau_s\right], \tag{3}$$

where $\langle\varepsilon\rangle = \dfrac{\langle E\rangle}{kT_\infty} \equiv \dfrac{\sum\limits_i \varepsilon_i \exp(-\varepsilon_i)}{\sum\limits_i \exp(-\varepsilon_i)}$.

The distribution function for molecules reflected from the particle surface, taking into account possible arbitrary accommodation of translational and internal energy, as well as a tangential impulse, has the form [8]

$$f_{ri} = f_{\infty i}\left[1 + A + B_1\left(c^2 - \frac{3}{2}\right) + B_2(\varepsilon_i - \langle\varepsilon\rangle) + Dc_\theta\right]. \tag{4}$$

The quantities A, B_1, B_2, and D, which depend on the polar angle θ, can be expressed in terms of the coefficient of vaporization (condensation) α_m, the coefficients of accommodation of translational α_E^{tr} and internal energy α_E^{int}, and the tangential impulse α_τ:

$$\alpha_m = \frac{|N^-| - |N^+|}{|N^-| - |N^W|}, \quad \alpha_E^{\mathrm{tr}} = \frac{(1-\alpha_m)\,|E_{\mathrm{tr}}^-| - |E_{\mathrm{tr}}^r|}{(1-\alpha_m)\,|E_{\mathrm{tr}}^-| - |E_{\mathrm{tr}}^W|},$$

$$\alpha_E^{\mathrm{int}} = \frac{(1-\alpha_m)\,|E_{\mathrm{int}}^-| - |E_{\mathrm{int}}^r|}{(1-\alpha_m)\,|E_{\mathrm{int}}^-| - |E_{\mathrm{int}}^W|}, \quad \alpha_\tau = \frac{(1-\alpha_m)\,|P_{r\theta}^-| - |P_{r\theta}^r|}{(1-\alpha_m)\,|P_{r\theta}^-|}.$$

The notation for the fluxes is standard [7]. The possibility for transformation of translational into internal energy and vice versa during collisions with the particle surface, which is characteristic of flows with subsonic velocities [7], is not taken into account in (4).

The only unknown parameter of the problem $\tau_s(\theta)$ is found from a solution of the stationary equation for heat conduction in the particle with boundary conditions such that the temperature is finite at the center of the particle and the heat integrated over the particle surface is balanced:

$$-\lambda_p \Delta T_p(r,\theta) = -\operatorname{div}\vec{I} = 2n\varkappa k_0\,|\vec{I}|\,B(r,\theta), \tag{5}$$

$$T_p|_{r\to 0} < \infty, \tag{6}$$

$$\int\left[(\vec{q}^- + \vec{q}^+)\,\vec{n}_r + L(N^- + N^+) + \sigma(T_s^4 - T_\infty^4) + \lambda_p\frac{\partial T_p}{\partial r}\right]_{r=R} dS = 0, \tag{7}$$

where $\vec{n}_r$ is the external normal to the particle surface; B(r, θ) is a dimensionless function that describes the distribution of energy in the electromagnetic field within the particle. Expressions for B(r, θ) are presented in [6] for small weakly and strongly absorbing particles.

The first term in (7) corresponds to transfer of heat into vapor due to heat conduction, the second is related to the latent heat of the phase transition, the third is related to emission from the particle surface, and the fourth is related to heat conduction in the volume of the particle.

It should be noted that in [6] the condition that gas molecules do not flow through the particle surface is used as the first boundary condition for the equation of heat conduction without any justification. It is not clear how this condition can affect the temperature distribution in the particle. In addition, the condition that the heat flux is continuous at each point of the particle surface is used in [6]. This made it necessary to resort in [6] to an unnatural technique involving the introduction of some average surface temperature for the particle. The approach used in the present work is free of this drawback. Condition (7) permits expressing the integration constant directly in terms of the known value of the temperature of the vapor in the unperturbed region T_∞.

The solution of Eq. (5) is sought as a sum of the general solution of the homogeneous Laplace equation and the particular solution of the inhomogeneous equation

$$T_p(r,\ \theta) = \sum_{l=0}^{\infty} a_l x^l P_l(\cos\theta) + \sum_{l=0}^{\infty} b_l x^{l+1} P_l(\cos\theta), \tag{8}$$

where $x = r/R$.

From (5)-(8), it follows that

$$\tau_s(\theta) = -\sum_{l=1}^{\infty} \frac{J_l I R}{\lambda_p T_\infty} P_l(\cos\theta) + \frac{J_0 I - K_1 \sqrt{\dfrac{2kT_\infty}{m}}\, P_\infty}{4\sigma T_\infty^4 + K_2 \sqrt{\dfrac{2kT_\infty}{m}}\, P_\infty}, \tag{9}$$

where

$$J_l = (2l+1)\, n\varkappa\rho \int_0^{\pi} P_l(\cos\theta) \sin\theta d\theta \int_0^{1} x^{l+2} B(x,\ \theta)\, dx;$$

$$K_1 = \alpha_m \left[\left(1 + \frac{\langle \varepsilon \rangle}{2}\right)(1+\nu_\infty)(\alpha_m - 2) + \left(1 + \frac{\langle \varepsilon \rangle}{2}\right)\exp(\gamma) + \alpha_E^{\mathrm{tr}}(1-\alpha_m)(1+\nu_\infty)\right];$$

$$K_2 = \frac{1}{2}\alpha_m \exp(\gamma)\left[1 + \frac{1}{2}(\langle \varepsilon \rangle - \beta) + (\beta - \gamma)(2 + \beta - \langle \varepsilon \rangle)\right] + (1-\alpha_m)\left[\alpha_E^{\mathrm{tr}} + \frac{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}{2}\alpha_E^{\mathrm{int}}\right].$$

According to (9), radiation from the particle surface can play an important role in forming the temperature field inside a nonvolatile ($\alpha_m = 0$) particle at very low pressures.

The total force acting on the particle equals the sum of the photophoretic force $\vec{F}_p$, the force due to light pressure $\vec{F}_{lp}$, and the resistance of the medium $\vec{F}_d$. The photophoretic force includes a light reactive component, related to the predominant evaporation from the more heated side of the particle.

The sum $\vec{F}_p + \vec{F}_d$ is determined by calculating the uncompensated impulse over the entire surface of the particle:

$$\vec{F}_{\mathrm{p}} + \vec{F}_{\mathrm{d}} = m\vec{n}_z \int dS \sum_i \sum_{\mp} \vec{d}v f_i^{\mp} V_z V_r. \tag{10}$$

The light pressure force $\vec{F}_{lp}$, according to [9], has the form

$$\vec{F}_{\mathrm{lp}} = k_{\mathrm{lp}} \pi R^2 \frac{\vec{I}}{c}, \tag{11}$$

where k_{lp} is the light pressure coefficient; c is the velocity of light.

The total force $\vec{F}$, taking into account (10)-(11), is

$$\vec{F} = 2\pi R^2 P_\infty \left[-\frac{J_1 R \vec{I}}{3\lambda_p T_\infty} K_3 + \frac{k_{\mathrm{lp}} \vec{I}}{2P_\infty c} - \vec{u}_\infty K_4\right], \tag{12}$$

where

$$K_3 = \frac{1}{2}\,\alpha_E^{\text{tr}}(1-\alpha_m) + \alpha_m \exp(\gamma)(\beta-\gamma);$$

$$K_4 = \frac{8}{3\sqrt{\pi}}\,[1+\alpha_m(\exp(\gamma)-1)] - \frac{4}{3\sqrt{\pi}}\,(1-\alpha_\tau)(1-\alpha_m)^2 + \frac{\sqrt{\pi}}{6}\,(1+\alpha_E^{\text{tr}})(1-\alpha_m) + \frac{5\sqrt{\pi}}{24}\,(1-\alpha_E^{\text{tr}})(1-\alpha_m)^2.$$

The velocity of the particle is determined from the condition $\vec{F} = 0$:

$$\vec{U} = \sqrt{\frac{2kT_\infty}{m}}\,\vec{I}\left[\frac{k_{1\text{p}}}{2P_\infty c} - \frac{J_1 R}{3\lambda_p T_\infty}\,K_3\right]/K_4. \tag{13}$$

It follows from (12)-(13) that the force on and velocity of the particle do not depend on the internal degrees of freedom of the gas molecules. This stems from the fact that the fraction of internal energy of the molecules, transmitted to the particle, averaged over the surface is compensated by the fraction of the particle energy going into excitation of internal degrees of freedom. The surface temperature distribution (9) depends on the magnitude of the average intramolecular energy and on the degree of its accommodation with collisions between the vapor molecules and the particle.

For complete accommodation, an equation that permits estimating the effect of the volatility of the particle on the photophoretic component of the velocity of motion follows from (13):

$$\frac{U_{\text{p}}(\alpha_m = 1)}{U_{\text{p}}(\alpha_m = 0)} \simeq \left(2 + \frac{\pi}{4}\right)\beta. \tag{14}$$

Since for most fluids, the quantity β is tens of units, apparently, the volatility can have a strong effect on the photophoretic motion of small drops in their own vapor (for water droplets $\beta \simeq 18$ at $T = 300°\text{K}$, $U_{\text{p}}(\alpha_m = 1)/U_{\text{p}}(\alpha_m = 0) \simeq 50$).

It is well known that due to the surface pressure, small drops can completely vaporize in a very short time in a saturated vapor. For this reason, it is useful to estimate the amount of supersaturation of the vapor necessary to compensate the surface pressure and to maintain a stationary regime. It is not difficult to show that for prolonged existence of a water drop with $R = 0.1$ μm without noticeable changes in its radius under irradiation with light with wavelength $\lambda = 1$ μm, $I = 0.84 \cdot 10^3$ W/cm^2 at $T_\infty = 300$ K and $\text{Kn} = l/R \simeq 10$, a supersaturation $\nu_\infty = (2\text{-}3)\cdot 10^{-2}$ is necessary. For low volatility substances (high value of β), conditions for quasistationary motion are also realized in a saturated vapor.

It follows from (13) that the direction of motion of the particle is determined by the signs of the so-called asymmetry factor of the temperature J_1 and of the denominator in expression (13). As shown in [6], the expression for J_1 is negative for both weakly and strongly absorbing particles. Analysis of the denominator in expression (13) showed that for any permissable values of α_m, α_E^{tr}, and α_τ, the denominator is positive. For this reason, a particle that is small compared to the wavelength of incident radiation in a free molecular regime can experience only positive photophoresis independent of its absorbing properties and volatility.

For submicron particles, it is necessary to consider the possibility of Brownian rotation and its effect on the motion of the particle. It is shown in [10] that the time for temperature relaxation of an irradiated particle at atmospheric pressure is $\tau \sim R^2/4\lambda_{\text{p}}$. For particles with $R = 0.1$ μm, $\tau \simeq 10^{-8}$. Within this time period, the particles has time to rotate only over a very small angle ($\simeq 1°$). For this reason, the effect of Brownian rotation on the motion of small particles in a radiation field can be neglected.

For a nonvolatile particle ($\alpha_m = 0$), in the case of a simple gas, the results obtained are comparable to the results in [6]. Since in the present work and in [6], different boundary conditions were used for the distribution function, such a comparison can be made only in a single particular case. For total accommodation ($\alpha_E^{\text{tr}} = \alpha_\tau = 1$), the results obtained in [6] follow from the expressions for the force (12) and velocity (13). For a strongly absorbing particle, the expressions for the photophoretic force and velocity agree with the results in [1-3], where the particle was modeled as an absolutely absorbing body.

NOTATION

λ, wavelength of the radiation; $\vec{I}$, intensity of the radiation; R, radius of the particle; l, average mean-free-path length for molecules in the gas; f_i^-, distribution function of the incident molecules; T_∞, temperature far away from the drops; n_∞, density of saturated vapor corresponding to it with a planar phase separation boundary; n_∞', actual density of the vapor far away from the particle; $\vec{u}_\infty$, dimensionless macroscopic velocity of the vapor far away from the particle; $\vec{v}$, dimensional molecular velocity; k, Boltzmann's constant; m, mass of a vapor molecule; E_i, internal energy of the i-th state of the molecule; f_i^+, distribution function of molecules emitted from the surface; f_{si}, distribution function of evaporated molecules; f_{ri}, distribution of reflected molecules; T_s, surface temperature of the particles; T_p, temperature inside the particle; α_m, coefficient of vaporization (condensation); n_s', density of saturated vapor at temperature T_s near the particle surface taking into account curvature; n_s, saturated vapor density for a planar phase boundary; σ^*, coefficient of surface tension for the particle substance; V_p, average volume per molecule of the liquid phase; α_E^{tr}, accommodation coefficient for translational energy; α_E^{int}, accommodation coefficient for internal energy; N^-, E_{tr}^-, E_{int}^-, and $P_{r\theta}^-$, fluxes corresponding to the number of particles, translational energy, internal energy, and tangential component of the momentum, stemming from incident molecules; N^+ and N^W, particle number of emitted and evaporated molecules; E_{tr}^W, and E_{int}^W, fluxes of translation and internal energy of reflected molecules, experiencing total thermal accommodation; λ_p, coefficient of thermal conductivity for the particle substance; N = n-in, complex index of refraction of the particle substance; $k_0 = 2\pi/\lambda$; $\vec{q}^-$ and $\vec{q}^+$, heat fluxes stemming from the incident and emitted molecules; σ, Stefan-Boltzmann constant; $\vec{F}_p$, photophoretic force; $\vec{F}_{lp}$, light pressure force; $\vec{F}_d$, drag of the medium; k_{lp}, light pressure coefficient; c, velocity of light in the medium; $\vec{U}$, velocity of the particle; Kn, Knudsen's number.

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