Comprehensive model of the photophoretic force on a spherical microparticle

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The photophoretic force is described by a comprehensive model containing aspects of both the optical local-field and gas-dynamic properties. It is shown that the model is in good agreement with detailed experimental data and provides a new means for measuring optical constants of microparticles.

Recently there has been a great deal of interest in the local field that is produced by electromagnetic radiation on the surface and within the interior of a microparticle.\(^1,2\) This interest is due, in part, to various enhancements that are found in photophysical interactions with molecular adsorbates, such as fluorescence\(^3\) and Raman scattering.\(^2\) Since such phenomena are generally observed in the far field, they principally provide information about the surface-averaged local field. Photophysical processes that directly measure the distribution of the local field are unknown to us. In this connection, the photophoretic force is of great interest, since its origin lies directly in the anisotropic heating process that is the result of a nonuniform local-field distribution. Pluchino\(^4\) has attempted to fit the size dependence of the radiometric force\(^5\) by incorporating Mie theory into the current continuum model of Yalamov et al.\(^6\) He found that although the model was in good qualitative agreement with theory, the measured force was found to be smaller than its calculated counterpart by 100 to 300%, depending on size. In what follows we show that Mie theory can account for the measured shape of the photophoretic force versus size so long as one is not restrained to continuum hydrodynamics and includes effects associated with the molecular mean free path in the external gas. This model is further tested by experimentally examining the dependence of the null point, i.e., the size at which the force on the particle vanishes before reversal, for various complex indices of refraction \(n\). Indeed, the results show that null-point measurements provide a means of obtaining the imaginary part of \(n\), a property not easily measured for particulates by any other technique.

In the limit of low Knudsen number (ratio of molecular mean free path to particle radius), a surface-temperature gradient \(\nabla T_s\) causes molecules at the surface to undergo a motion in the direction of the gradient known as Maxwellian creep.\(^7\) At the surface of a sphere, this creep velocity is given by

\[
V_\theta = \frac{K_\eta_e}{R T_s \rho_g} \frac{\partial T_s}{\partial \theta},
\]

where \(K\) is the coefficient of thermal slip, \(T_s\) is the surface temperature, \(R\) is the particle radius, \(\rho_g\) is the density of the external gas, \(\eta_e\) is the gas viscosity, and angle \(\theta\) is defined in Fig. 1. The stress imparted to the gas by the unevenly heated surface produces a reaction on the surface that is the origin of the photophoretic force (photothermal) in the small-Knudsen-number regime. Yalamov et al.\(^3\) have shown by applying such a stress to the surface that the resulting force \(F_r\) is

\[
F_r = -\frac{4 \pi R_\eta_e^2 J K I}{\rho_g T s K_i},
\]

where \(K_i\) is the interior thermal conductivity, \(I\) is the incident intensity, and \(J\) is a measure of the asymmetry of the internal heat sources. This asymmetry factor is

![Fig. 1. Coordinate system used in evaluating Eqs. (1) and (3).](image-url)
actually a composite of two dimensionless factors, the well-known absorption efficiency \( Q_a \) and an anisotropy factor \( A_2 \), \( J = \frac{3}{8} Q_a A_2 \). This anisotropy factor, which provides a measure for the distribution of the absorbed energy, is given by

\[
A_2 = \frac{\int_0^1 dx' x'^3 \int_0^\pi d\theta \sin(2\theta) |E_i(x', \theta)|^2}{\int_0^1 dx' x'^2 \int_0^\pi d\theta \sin \theta |E_i(x', \theta)|^2},
\]

where \( x' \) is the dimensionless length \( r/R \) and \( |E_i(x', \theta)|^2 \) is the square modulus of the internal electric-field strength averaged over the azimuthal angle \( \phi \). It is \( A_2 \) that controls the sign of the force; with \( A_2 \) positive, the back surface is heated most effectively, and the particle moves back toward the light source (negative photophoresis). Equation (2) has been applied to the measurement of the photophoretic force on a slowly evaporating glycerol drop; the intensity was low enough that the force was not affected by any photothermally induced evaporation. The resulting value of \( J \) as reported by Arnold and Lewittes is shown by the lower curve in Fig. 2. The points in the same figure show the results of a calculation by Pluchino. As one can see, the agreement is qualitative except for the position of the crossover point and the sizes corresponding to the apparent resonances in this spectrum. Experimental explanations for this difference, such as the use of a Gaussian beam or improper intensity calibration, have been ruled out in the interim. This disparity is more fundamental. The model of Yalamov et al. applies only to the case of low-Knudsen-number, continuum theory. Although the mean free path was smaller than 10% of the diameter for the experimental results in Fig. 2, we now look at its possible significance.

Reed has evaluated the effect on photophoresis of the breakdown of continuum hydrodynamics through the use of phenomenological transport coefficients. However, in his work the particle was assumed to be surface absorbing [i.e., \( |E(r, \theta)|^2 = |E(\alpha, \pi)|^2 H(\pi/2 - \theta \cos \theta) \)]. In either case, Reed showed that the force should be reduced from the continuum result by a factor

\[
g(K_n) = \frac{1}{1 + 3C_m K_n} \frac{1}{1 + 2C_t K_n}, \tag{4}
\]

where \( C_m \) is related to momentum accommodation at the gas–particle interface (a number between 1.00 and 1.35) and \( C_t \) is the temperature-jump coefficient (a number between 1.875 and 2.48). In contrast to the findings of Reed, our internal electromagnetic field includes all appropriate vector spherical harmonics in the source function Mie theory. However, this does not preclude the use of Eq. (4). When one considers that only the first Legendre term in the surface-temperature distribution drives the force, the role of the Mie theory is principally one of determining the amplitude of this component. Once having done this, we essentially return to Reed’s problem. Thus Eq. (4) will be incorporated as a multiplication factor into the continuum model

\[
F_{rc} = F_{rg}(K_n). \tag{5}
\]

Using typical numbers for \( C_t \) and \( C_m \) (2.0 and 1.0, respectively) we arrive at the result shown by the top curve in Fig. 1. The agreement is now very good; however, it involves one adjustable constant. The constant is \( K \), Maxwell’s so-called thermal slip coefficient. It is significant that the value of \( K \) needed in producing the agreement in Fig. 2 is \( \approx 1.25 \) and not \( 3/4 \) as predicted by Maxwell. Some variation in \( K \) may be produced by choosing slightly different values of \( C_t \) and \( C_m \). However, within the normal range of these constants, \( K \) is not reduced by more than 15%. Apparently the disparity between our value and that given by Maxwell requires a more enlightened understanding of the effects of surface scattering on the thermally induced molecular flow field around the particle. Derjaguin and Yalamov have looked at this problem theoretically and find values from 0.75 to 1.5, depending on the degree of
diffuseness in the molecular scattering process. Accordingly, our value indicates that a significant percentage of scattering events are diffuse. A further test of Eq. (5), which does not depend on either the transport properties in the particle or the surrounding gas, involves the determination of the null point.

Figure 3 shows the experimental setup for null-point measurements. The particle is stably trapped in the levitator normally used for photophoretic spectroscopy. A disk electrode within this chamber produces a centering force. The particle is sized as in Ref. 5 by producing a shadow image using the forward-scattered light from a He–Ne laser. A square-wave-modulated beam from a tunable CO₂ laser is introduced horizontally, causing the particle to move toward or away from the laser source. At large sizes the particle is pushed, as it shrinks; eventually the force is reversed and the particle is pulled just beyond the null point. This point of reversal is revealed, and visually detected, by a change in phase of 180° of the horizontal fluctuation with respect to the laser modulation.

The results at three distinct wavelengths are shown in Table 1. The refractive indices were obtained from bulk measurements. We see agreement within the uncertainty in size at 10.63 and 10.22 μm. However, the theoretical null point is slightly outside our experimental uncertainty in size at 10.33 μm. If we consider the uncertainty in the measurement of K at this wavelength, a calculated value consistent with the measurement is obtained.

We have shown that photophoresis may be described by a comprehensive model that includes Mie theory and a realistic view of mean-free-path effects. Furthermore, we have demonstrated that the supposition that the imaginary part of the refractive index for a single particle may be measured from the null point is in fact correct. Data that are taken in the IR may be expected to be scaled to smaller particles in the visible. Thus reversed levitation of a spherical particle 1 μm in diameter, with equivalent visible refractive index, was predicted to occur on the basis of the original model at one solar constant. However, the mean-free-path correction in Eq. (5) considerably reduces the force, negating the possibility of spherical particle levitation under terrestrial conditions. In applying our linear model to atmospheric particles, such as sulfuric acid droplets, carbon soot, and desert dust, no levitation from solar irradiation is found. This statement does not include nonspherical particles, for which calculations have not been made. Contrary to our findings, Sitarski and Kerker find that for large Knudsen numbers some of these atmospheric particles will be levitated by solar irradiation.

It is interesting to note that our model was recently applied to the surface-mode region of small particles. We see in this case that photophoresis allows one to detect high-order surface modes that are not readily addressed by light scattering. These modes are revealed by an enhancement in A₂.

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**Table 1. Photophoretic Null-Point Measurement**

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<th>k</th>
<th>x</th>
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References