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THERMOPHORETIC VELOCITY
OF LARGE AEROSOL PARTICLES

A. K. Postma

November, 1965

BATTELLE-NORTHWEST

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THERMOPHORETIC VELOCITY OF LARGE AEROSOL PARTICLES

INTRODUCTION

The phenomenon of thermal repulsion of particles suspended in gases has received extensive investigation, both theoretically and experimentally. In the theoretical approaches, the particles have been considered as either large or small compared to the molecular mean free path. The intermediate region where particle size is comparable with the mean free path, ℓ , has so far proved too complex for theoretical treatment. In this work we will restrict our attention to particles much larger than the mean free path, where the Navier-Stokes equations are known to be applicable.

The theoretical calculations of the thermal forces for large particles have been carried out under the assumption that the particle remained stationary with respect to the fluid far from the particle.^[1,2] The observed phenomenon, thermal deposition, results from the motion of the particle caused by the thermal force; hence, the velocity of this motion is of prime interest. Previously the velocity of thermal repulsion has been calculated by equating the thermal force exerted on a stationary particle to the viscous force arising from the particle motion.

The viscous force equation is based on boundary conditions which allow for fluid slip at the surface in proportion to the local shear stress at the surface. In the case of thermal motion, there is an additional tangential fluid velocity at the surface. Depending on the position, the magnitude of this thermal velocity varies from zero to a maximum whose value is greater than the velocity of thermal repulsion. Thus, as has been noted by Saxton and Ranz^[3] and Schadt and Cadle^[4], the analysis in which the Stokes-Cunningham drag force is equated to the thermal force exerted on a stationary particle is theoretically unsound. This is so because the equation for the viscous force is based on boundary conditions which do not apply when the sphere is under the influence of a temperature gradient. In addition to this difference in boundary conditions, there is no a priori reason to assume that the thermal force is independent of the particle motion.

Nevertheless, it has been determined experimentally that the thermophoretic

velocity is in agreement with the value predicted by equating the thermal force on a stationary sphere to the viscous force calculated from the particle mobility in the absence of a thermal gradient^[3,4,5]. This observed agreement is surprising in view of the discrepancy in the boundary conditions noted above.

OBJECTIVE

It is the purpose of this work to derive the equation of thermal force, allowing for a relative velocity, u , between the particle and the gas stream. The velocity of thermal repulsion will be the value of u for which the total force acting on the sphere vanishes. The range of applicability of the analysis will be investigated by comparison with available experimental data.

SUMMARY

The velocity of thermal repulsion of large aerosol particles has been calculated by others by equating the thermal force on a stationary particle to the Stokes-Cunningham viscous force. This procedure is theoretically unsound because the boundary conditions employed in the viscous force equation are erroneous when the particle moves in a thermal gradient. In the current study these difficulties have been circumvented by rederiving the thermal force equation, allowing for a relative velocity between the particle and the gas stream. The velocity of motion is then calculated by setting the net force on the particle equal to zero.

The velocity obtained by this more realistic approach agrees with that calculated by the former method, which is surprising in view of the incorrect boundary conditions employed in the former method. Investigation of the drag force equation shows that the thermal force and the viscous force are exerted independently of each other, which explains this unexpected agreement. The range of applicability of the analysis is explored by comparison with available experimental data.

THERMAL FORCE

Consider a sphere of radius, a , suspended in a gas stream in which a uniform temperature gradient exists in the z direction at large distances from the sphere. At large distances from the sphere, there is a uniform flow of gas in the z direction. The flow system is shown schematically in Figure 1.

FIGURE 1
SCHEMATIC SKETCH OF FLOW SYSTEM

The net aerodynamic force acting on the sphere in the positive z direction is

$$F = \int_s (-P \cos \theta + \tau_{rr} \cos \theta - \tau_{r\theta} \sin \theta) ds, \quad (1)$$

where the integration is carried out over the surface, s . P represents the pressure, τ_{rr} is the normal shear stress, and $\tau_{r\theta}$ is the tangential shear stress. Before the integration can be carried out, the three stresses must be determined in terms of the position coordinates.

General equations for the velocity profile around a sphere for the case of axial symmetry are given by Lamb^[6] as

$$u_r = \left(U - \frac{2A}{r^3} - \frac{2B}{r} \right) \cos \theta \quad (2)$$

$$u_{\theta} = -(U + \frac{A}{r^3} - \frac{B}{r}) \sin \theta \quad (3)$$

in which the constants, A and B, are to be determined from the boundary conditions. u_r and u_{θ} are the velocity components in the r and θ directions, respectively.

The pressure distribution can be obtained by substituting the velocity profile, Equations 2 and 3, into the momentum equations for creeping flow.^[7] Neglecting field forces, this substitution results in

$$P = -\frac{2\mu B}{r^2} \cos \theta, \quad (4)$$

where μ = gas viscosity.

The normal shear stress is

$$\tau_{rr} = 2\mu \frac{\partial u_r}{\partial r} = (\frac{12A}{r^4} + \frac{4B}{r^2}) \mu \cos \theta \quad (5)$$

and the tangential shear stress is

$$\tau_{r\theta} = \mu \left[\frac{1}{r} \frac{\partial u_r}{\partial \theta} + \frac{\partial u_{\theta}}{\partial r} - \frac{u_{\theta}}{r} \right] = \frac{6\mu A}{r^4} \sin \theta. \quad (6)$$

Substituting Equations 4, 5, and 6 into Equation 1 and carrying out the integration, we find for the net drag force,

$$F = 8\pi\mu B. \quad (7)$$

The boundary conditions which apply at the surface of the sphere are

$$u_r = 0 \quad (8a)$$

and

$$u_{\theta} = C_m \left\{ r \frac{\partial}{\partial r} \left(\frac{u_{\theta}}{r} \right) + \frac{1}{r} \frac{\partial u_r}{\partial \theta} \right\} + \frac{3}{4} \frac{\mu}{\rho T} \frac{1}{a} \left(\frac{\partial T_f}{\partial \theta} \right) \quad (8b)$$

at $r = a$

where

C_m = a constant related to the slip at the surface

ℓ = mean free path of gas molecules

ρ = gas density

T = average absolute temperature near particle

T_f = gas temperature.

The first boundary condition, Equation 8a, merely states that there is no gas flow into the sphere. The second boundary condition, Equation 8b, prescribes the tangential velocity at the surface of the sphere; and allows for both a viscous slip and a thermal flow. The form of the viscous slip term, $C_m \ell \left[r \frac{\partial}{\partial r} \left(\frac{u_\theta}{r} \right) + \frac{1}{r} \frac{\partial u_r}{\partial \theta} \right]$, may be interpreted as stating that the slip is proportional to the shear stress. For small values of $\frac{\ell}{a}$, the viscous force predicted from this intuitive method of handling slip agrees with the force calculated by Epstein^[8] on the basis of kinetic theory. The velocity of thermal creep, $\frac{3}{4} \frac{\mu}{\rho T} \frac{1}{a} \left(\frac{\partial T_f}{\partial \theta} \right)$, is that deduced by Maxwell on the basis of molecular impingement calculations. As Brock^[2] points out, Epstein, in his radiometer theory, neglected the viscous slip.

The gas temperature must be obtained by solving the energy transport equation. Since the velocities are very small, the convective terms in the energy transport equation will be neglected, so that we must solve Laplace's equation:

$$\nabla^2 T_f = \nabla^2 T_s = 0 \quad (9)$$

where T_s = temperature of solid sphere. The boundary conditions are:

$$k_f \left(\frac{\partial T_f}{\partial r} \right) = k_s \left(\frac{\partial T_s}{\partial r} \right) \quad \text{at } r = a \quad (10)$$

and

$$T_f - T_s = C_t \ell \left(\frac{\partial T_f}{\partial r} \right) \quad \text{at } r = a \quad (11)$$

where

k_f = thermal conductivity of fluid

k_s = thermal conductivity of solid particle

C_t = constant.

Equation 10 is based on energy conservation, and Equation 11 is the relationship between the fluid temperature, T_f , and the particle temperature evaluated

at the particle surface. The quantity, C_t is a coefficient whose value depends on the nature of the interaction of the gas molecules with the particle surface. Good treatment of the temperature jump at an interface may be obtained from References 9 and 10. Since precise values of C_t cannot be calculated theoretically, C_t must be regarded as an empirical constant. The solution to Equation 9 which satisfies Equations 10 and 11 is

$$T_f = g r \cos \theta + \frac{a^3 g \left(\frac{k_f}{k_s} - 1 + C_t \frac{\ell}{a} \right) \cos \theta}{r^2 \left(1 + 2 \frac{k_f}{k_s} + 2C_t \frac{\ell}{a} \right)} \quad (12)$$

where g is the magnitude of the temperature gradient. Combining Equations 7, 8, 10, 11, and 12 gives for the force on the particle

$$F = \frac{4\pi\mu a}{\left(1 + 3C_m \frac{\ell}{a}\right)} \left\{ -\frac{2}{4} \frac{\mu g}{\rho T} \frac{\left(\frac{k_f}{k_s} + C_t \frac{\ell}{a}\right)}{\left(1 + 2 \frac{k_f}{k_s} + 2C_t \frac{\ell}{a}\right)} + U \left(\frac{3}{2} + 3C_m \frac{\ell}{a} \right) \right\} \quad (13)$$

The velocity of thermal repulsion is the value of U for $F = 0$:

$$U = \frac{3}{2} \frac{\mu g}{\rho T} \frac{\left(\frac{k_f}{k_s} + C_t \frac{\ell}{a}\right)}{\left(1 + 2C_m \frac{\ell}{a}\right) \left(1 + 2 \frac{k_f}{k_s} + 2C_t \frac{\ell}{a}\right)} \quad (14)$$

DISCUSSION

The final equation for the thermal force contains two constants, C_m and C_t , whose values must be determined before numerical values of the thermal repulsion velocity can be calculated. The constant, C_m , related to the viscous slip may be evaluated from measurements of settling velocity in the absence of temperature gradients. According to Equation 13, the drag force in the absence of a thermal gradient is

$$F = \frac{6\pi\mu a U \left(1 + 2C_m \frac{\ell}{a}\right)}{\left(1 + 3C_m \frac{\ell}{a}\right)} \quad (15)$$

From kinetic theory considerations, Epstein^[8] was able to derive an equation of the form proposed earlier by Cunningham for the viscous force on a sphere. This equation is

$$F = \frac{6\pi\mu aU}{1 + A_m \frac{\ell}{a}} \quad (16)$$

In Equation 16, A_m is the accommodation coefficient, and its value depends on the degree of momentum transfer achieved by the molecules impinging upon the surface. Epstein^[8] obtained the following formula for A_m :

$$A_m = 0.998\left(\frac{2}{\alpha} - 1\right) \quad (17)$$

where α denotes the fraction of gas molecules undergoing diffuse reflection at the surface, and $1-\alpha$ denotes the fraction undergoing specular reflection. Experimentally, Millikan^[12] found $A_m = 1.23$ for oil drops which corresponds to about 10 per cent of the molecules being reflected specularly. For other surfaces and gases, the experimentally observed values of α fall between 0.8 and 1.0.^[12]

Since the forces in Equations 15 and 16 must be identical, the relationship between C_m and A_m is

$$C_m = \frac{A_m}{1 - 2A_m \frac{\ell}{a}} \quad (18)$$

For very small $\frac{\ell}{a}$ values, A_m is practically identical to C_m . However, as $\frac{\ell}{a}$ approaches a value of ~ 0.4 , C_m becomes very large showing that the continuum approach has completely failed at this $\frac{\ell}{a}$.

Simple arguments based on kinetic theory^[9] give the value for C_t

$$C_t = \frac{2(2 - A_t)}{A_t(\gamma + 1)} \frac{k_f}{\mu C_v} \quad (19)$$

where

A_t = thermal accommodation coefficient

k_f = thermal conductivity of gas

μ = gas viscosity

C_v = heat capacity of gas at constant volume

γ = heat capacity ratio, C_p/C_v .

The thermal accommodation coefficient is analogous to the momentum accommodation coefficient A_m . Numerically, A_t represents the fraction of incident molecules which achieve complete thermal equilibrium with the surface, and $1-A_t$ represents

the fraction which transfer no thermal energy to the surface. Unfortunately, the wide range of reported values^[13] of the thermal accommodation coefficient, A_t , prevents any general statement of the value of C_t . Hence, for the present, C_t must be regarded as a constant whose value must be obtained from experimental measurements on the system of interest.

For comparison purposes, a thermophoretic velocity may be computed by equating the thermal force on a stationary particle to the Stokes-Cunningham viscous force. The final expression for this velocity is

$$U = \frac{3\mu g(1 + A_m \frac{\ell}{a})(\frac{k_f}{k_s} + C_t \frac{\ell}{a})}{2\rho T(1 + 3C_m \frac{\ell}{a})(1 + 2 \frac{k_f}{k_s} + 2C_t \frac{\ell}{a})} . \quad (20)$$

When the relation between A_m and C_m , given by Equation 18, is taken into account, Equation 20 is identical to Equation 14, obtained by allowing for the particle motion. This agreement shows that the discrepancy in boundary conditions noted earlier does not lead to an error in the calculated velocity of thermal repulsion; hence, the observed^[3,4,5] agreement between the thermal force measured statically and that calculated from the Stokes-Cunningham is explained theoretically.

The reason for this agreement may be seen from an examination of Equation 13, which may be stated

$$\text{Net Force} = \text{Thermal Force} + \text{Viscous Force} \quad (13a)$$

As may be noted from Equation 13, the thermal force in Equation 13a is independent of the velocity with which the sphere moves. Likewise, the viscous force is independent of the thermal gradient. Equating the thermal force on a stationary sphere to the Stokes-Cunningham viscous force is equivalent to writing Equation 13 with $F = 0$, which correctly gives the thermophoretic velocity. Thus, the unexpected agreement noted above results from the fact that the thermal force and viscous force are independent of each other.

REGION OF APPLICABILITY

The analysis used in this study was based on the use of the Navier-Stokes equations, which are applicable only when the fluid can be considered a continuum. The actual value of $\frac{\ell}{a}$ at which the continuum analysis breaks down is best determined by comparing the theoretical predictions with experimental measurements.

In Figure 2, Equation 13 (with $U = 0$) is compared with experimental measurements of thermal force on tricresylphosphate as reported by Rosenblatt and LaMer^[15] and by Schadt and Cadle.^[4] The value of A_m was taken as 1.23, which is the value found by Rosenblatt and LaMer^[5] for tricresylphosphate drops. The value of C_t was chosen as 2.5 because this value gives the best agreement with the experimental results at small $\frac{l}{a}$ values.

Inspection of the figure shows that the slip flow analysis agrees very well with the experimental measurements for $\frac{l}{a}$ values up to about 0.13. If we arbitrarily set $A_m = C_m$ for all $\frac{l}{a}$ as Brock^[2] does, the theoretical curve appears to agree with the experimental measurements up to $\frac{l}{a}$ of approximately 0.3. It must be recognized that the formula based on $A_m = C_m$ is theoretically sound only where $2A_m\frac{l}{a}$ is negligible compared to unity. Thus, neglecting this term amounts to an empirical change in the hydrodynamic theory.

In Figure 3, Equation 13 (with $U = 0$) is compared to the measurements by Schadt and Cadle^[4] on sodium chloride particles. Unfortunately, the experimental measurements do not extend into the region of applicability of the continuum analysis. However, if data are extrapolated into the region of smaller $\frac{l}{a}$ values, the extrapolated data do fall on the theoretical curve. This rather unsatisfactory comparison does serve as an indication that the theory satisfactorily accounts for the thermal conductivity of the particle and the gas.

The magnitude of the thermal velocity is generally small. For illustration purposes, the velocity of thermal repulsion for particles in air at room conditions is plotted in Figure 4. For particles larger than one micron, $\frac{l}{a}$ is less than 0.13, so that the continuum analysis applies. For particles smaller than 0.02 μ diameter, $\frac{l}{a}$ is greater than 3, where, according to Schmitt's^[14] experiments, Waldmann's theory^[15] applies.

Between these two extremes there is an intermediate region where a satisfactory theory has not yet been formulated. The dashed lines drawn in this region are based on intuitive interpolation and must be regarded as such. The values of C_t and A_m were chosen as 2.5 and 1.23, respectively, because these values were found to be applicable for the tricresylphosphate drops and the sodium chloride particles.

FIGURE 2

COMPARISON OF THEORY WITH MEASUREMENTS ON TRICRESYLPHOSPHATE DROPS

FIGURE 3
COMPARISON OF THEORY WITH MEASUREMENTS ON
SODIUM CHLORIDE PARTICLES

FIGURE 4. THERMOPHORETIC VELOCITY IN AIR AT 1 ATM. AND 70 °F
Thermal Gradient = 100 °K/cm

CONCLUSIONS

The thermophoretic velocity of aerosols having a particle diameter greater than about 14 times the mean free path of the gas molecules can be computed if the fluid is assumed to be a continuum. The slip flow analysis appears to correctly predict the effect of thermal conductivity over the entire conductivity range. The velocity of thermal repulsion obtained by equating the thermal force on a stationary particle to the Stokes-Cunningham viscous force is identical to that predicted when proper allowance for the particle motion is made.

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