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PHORETIC AND RADIOMETRIC FORCE MEASUREMENTS ON MICROPARTICLES IN MICROGRAVITY CONDITIONS

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ABSTRACT

Thermophoretic, diffusiophoretic and radiometric forces on microparticles are being measured over a wide range of gas phase and particle conditions using electrodynamic levitation of single particles to simulate microgravity conditions. The thermophoretic force, which arises when a particle exists in a gas having a temperature gradient, is measured by levitating an electrically-charged particle between heated and cooled plates mounted in a vacuum chamber. The diffusiophoretic force arising from a concentration gradient in the gas phase is measured in a similar manner except that the heat exchangers are coated with liquids to establish a vapor concentration gradient. These phoretic forces and the radiation pressure force acting on a particle are measured directly in terms of the change in the dc field required to levitate the particle with and without the force applied. The apparatus developed for the research and the experimental techniques are discussed, and results obtained by thermophoresis experiments are presented. The determination of the momentum and energy accommodation coefficients associated with molecular collisions between gases molecules and particles and the measurement of the interaction between electromagneic radiation and small particles are of particular interest.

INTRODUCTION

In the absence of gravity, a number of forces on small particles can be the dominant force leading to particle movement and deposition on surfaces. Such forces may be undesirable for containerless processing and other applications. A small particle exposed to an external temperature gradient will experience a thermophoretic force as a result of differences in momentum transferred to the particle by the gas molecules colliding with the particle from the hot and cold sides. This principle is the basis of the thermopositor, which is used to deposit aerosol particles from a gas stream onto a cold surface, and is used in the modified chemical vapor deposition (CVD) process for optical fiber production (Morse *et al.*, 1985). The deposition of soot and carbonaceous particles on colder surfaces in contact with a hot gas can be an undesired result of thermophoresis. The thermophoretic force has been used to prevent particles from depositing on wafer surfaces in the micro-electronics industry (Ye *et al.*, 1991; Bae *et al.*, 1994; Lee *et al.*, 1996). As indicated in the extensive surveys of thermophoresis and diffusiophoresis by Waldmann and Schmitt (1966) and by Derjaguin and Yalamov (1972), there exists a large literature on the theories of phoretic phenomena, but there remains a paucity of high-quality data.

The need for experimental data is absolute, for existing theories require knowledge of accommodation coefficients and other coefficients to predict the relevant force. Maxwell (1879) recognized and addressed this problem early in his development of the kinetic theory of gases, and he introduced the concept of partial accommodation of gas molecules with a surface. Momentum and energy are exchanged by molecular collisions, and the possible extent of the interaction ranges from reflection (specular emission) to complete accommodation (diffuse emission) with the surface. Accommodation coefficients for momentum and energy may be defined by

$$\alpha_m = (M_i - M_e)/(M_i - M_s) \text{ and } \alpha_t = (E_i - E_e)/(E_i - E_s) \qquad [1]$$

Here M represents the average tangential components of the momentum of molecules, and E is the average energy flux. Subscripts e, i and s refer, respectively, to molecules emerging from the surface, incident molecules, and molecules leaving in Maxwellian equilibrium with the surface.

Application of kinetic theory represents one of three approaches to the theories of thermophoresis and diffusiophoresis which have been taken: (i) continuum theory and deviations from continuum theory due to slip, (ii) solutions based on linearization of the Boltzmann equation, and (iii) semi-theoretical models. When the mean free path, ℓ, of the gas molecules is small compared with the radius, a, of a spherical aerosol particle, that is, when the Knudsen number, Kn, is small ($Kn = \ell/a << 1$), continuum theory applies. As the Knudsen number increases, discontinuities in the temperature and gas velocity occur near the surface, and slip models have been used to account for the deviations from continuum theory. When $Kn >> 1$, gas molecules colliding with the surface can be in the free-molecule regime and have a Maxwell-Boltzmann distribution of molecular velocities.

Rigorous analysis of the thermophoretic force for arbitrary Knudsen number is fraught with difficulty. Determination of the molecular velocity distribution function requires solution of the Boltzmann equation with appropriate boundary conditions. One solution that looks promising is that of Loyalka (1992), who developed a scheme for the solution of the linearized form of the Boltzmann equation, which he used to perform computations of the thermophoretic force for hard spheres. Little is known about the phoretic forces on nonspherical particles.

The interaction between small particles and electromagnetic radiation is well-understood for small spheres, for Mie theory can be applied to microspheres illuminated by a monochromatic planar wave, provided that the optical properties (size and complex refractive index) of the particle is known. For crystalline particles and other small masses having an irregular shape, electromagnetic scattering theory is not yet adequate to predict the radiation pressure force, and yet crystalline particles and amorphous particles are more likely to be encountered in applications than spherical particles.

OBJECTIVES

The primary objective of this research is to make precise measurements of phoretic and radiometric forces on microparticles. The phoretic force data on microspheres will be analyzed to determine accommodation coefficients and slip coefficients needed to predict phoretic phenomena. Radiometric force data will be used to determine the optical properties of carbonaceous particles such as soot and other contaminants. Measurements of phoretic forces on particles of irregular shape will be used to determine the effects of particle morphology and rotational motion on gas/particle interactions.

THEORETICAL BACKGROUND

In analyses of the free molecule regime ($Kn >> 1$) it is usually assumed that the velocity distribution function of molecules colliding with the particle is not disturbed by the particle. Based on the Chapman-Enskog distribution function for a non-uniform gas, Waldmann (1959) developed the following equation for the thermophoretic force on a sphere

$$\mathbf{F}_{fm} = -\frac{32}{15} a^2 \frac{k_{tr}}{\bar{c}} \nabla T_\infty , \qquad [2]$$

in which k_{tr} is the translational part of the thermal conductivity of the gas, ∇T_∞ is the external temperature gradient in the region unperturbed by the particle, and $\bar{c}$ the mean molecular speed given by

$$\bar{c} = \sqrt{8kT/\pi m} \, . \qquad [3]$$

Here k is Boltzmann's constant, and m is the molecular mass.

An analogous theory in terms of the vapor concentration gradient applies to diffusiophoresis.

The near-continnum regime or slip flow regime ($Kn < 0.1$) was first analyzed by a slip flow model by Epstein (1929), who solved the Navier-Stokes equations and Laplace's equation for the temperature field, taking into account thermal slip at the gas/particle boundary. Recognizing that experimental evidence did not support Epstein's theory, Brock (1962) extended the analysis to include the velocity slip and temperature jump boundary conditions. His result may be written in the form

$$\mathbf{F}_{th} = -6\pi a^2 (0.499) \rho \bar{c} \sigma \frac{k_2}{p} Kn\, \gamma(c_m Kn)\, \delta(k_1, k_2, c_t Kn) \nabla T_\infty . \qquad [4]$$

Here γ is a function of the product $c_m Kn$, where c_m is a velocity slip constant, and δ is a function of $c_t Kn$ and the thermal conductivities of the sphere and gas, k_1 and k_2, respectively. Here c_t a temperature jump constant, and the phenomenological coefficient σ accounts for tangential thermal slip. The constants c_m and c_t are related to the momentum and thermal accommodation coefficients.

The intermediate or Knudsen regime ($Kn \sim 1$) is much more difficult to analyze than the continuum and free-molecule regimes. An example of a theoretical anaylsis is Dwyer's (1967) application of the 13-moment method of Grad to obtain an equation to third order in Kn of the form

$$\mathbf{F}_{th} = -\frac{16}{15} \pi a^2 \frac{k_2}{\bar{c}} \Big\{ c_t Kn^2 + \Big[\frac{1 + 2k_2/k_1}{c_m(12\,Kn + \alpha_t)} + \frac{k_2}{k_1} \Big] Kn + \frac{2c_t Kn}{(12c_m Kn+1)\Big[\frac{6c_t}{15} Kn^3 + \big(\frac{1}{5} - \frac{3R\mu}{2k_1}\big) Kn^2 + \frac{1}{3}\big(1 + \frac{2k_2}{k_1} + 2Kn\pi c_t\big)\big(\frac{3c_m Kn+1}{12c_m Kn+1}\big)\Big]} \Big\} \nabla T_\infty . \qquad [5]$$

Note that coefficients c_m, c_t, α_m and α_m all appear in the equation.

The more recent analysis of Loyalka (1992) based on solution of the Boltzmann equation does not result in a closed form solution.

APPARATUS & TECHNIQUES

Direct measurements of phoretic forces are being measured by stably levitating single droplets and particles electrodynamically. Davis (1992) reviewed the principles and applications of electrodynamic trapping. As shown in Figure 1, a double-ring EDB of the type analyzed by Davis *et al.* (1990) is mounted in a stainless steel vacuum chamber for thermophoresis studies. Parallel stainless steel rings are mounted above and below the midplane of the balance. When the levitated particle is positively charged, the potentials applied to the top and bottom electrodes are, respectively

$$V_t = - V_{dc} + V_{ac}\cos\omega t, \text{ and } V_b = + V_{dc} + V_{ac}\cos\omega t, \qquad [6]$$

in which $\omega = 2\pi f$ is the circular frequency of the ac source having frequency f, $2V_{dc}$ is the levitation voltage, and V_{ac} is the amplitude of the ac potential.

The ac field exerts no time-average force on the particle, so the dc field balances the gravitational force and any other vertical force F_z, according to the equations

$$qC_o \frac{V_{dc,o}}{z_o} = - mg, \text{ and } qC_o \frac{V_{dc}}{z_o} = - mg + F_z \qquad [7]$$

where q is the coulombic charge on the particle, C_o and z_o are geometrical constants, m is the particle mass, and g is the acceleratin of gravity.

Solving for F_z using Eq. [7], we obtain

$$\frac{F_z}{mg} = 1 - \frac{V_{dc}}{V_{dc,o}} = - \frac{\Delta V}{V_{dc,o}} = \frac{V_{dc} - V_{dc,o}}{V_{dc,o}} . \qquad [8]$$

Thus, the ratio of the thermophoretic force to the particle weight is obtained by making two voltage measurements. First, the levitation voltage is recorded in the absence of the force of interest, and then after the force is applied. By varying the pressure in the vacuum chamber and repeating the voltage measurements, the phoretic force can be determined as a function of the Knudsen number.

Identical hollow copper chambers (pillboxes) are mounted above and below the electrodes to generate a temperature gradient. Each chamber is connected to a constant temperature bath. The upper cell can be operated in the range 0° to 120°C, and the lower cell range is -40° to 120°C. In experiments the upper cell is maintained at a higher temperature than the lower cell to minimize or eliminate natural convection. Natural convection can only be totally eliminated by operating the entire apparatus in a microgravity environment.

A laser beam enters horizontally through a window in one of the access ports, and a 512 pixel photodiode array is mounted at the exit of a second port to measure the phase function (scattered intensity as a function of angle) of a levitated sphere.

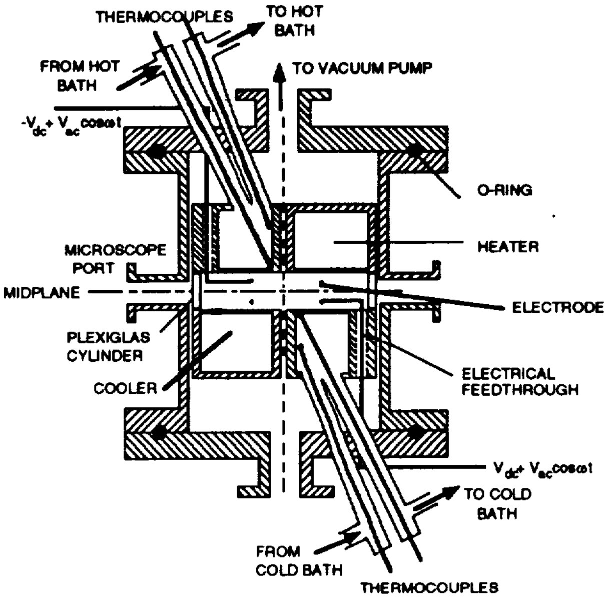

Figure 1. The apparatus used for thermophoresis studies.

EXPERIMENTAL RESULTS

For all of the experiments for which Kn exceeded 3 a decrease in the thermophoretic force was observed. The apparent decrease in the thermophoretic force arises because the temperature gradient used in the computation of the ordinate is not the effective temperature gradient for large values of Kn. As the mean free path of the gas approaches the distance between the heated and cooled plates, the temperature gradient at the center of the chamber deviates from the assumed continuum value, for there are temperature jumps at the solid surfaces. There is a second Knudsen number, $Kn_2 = \ell/H$, which must be taken into account in the interpretation of the data. Devienne (1965) proposed the following correction to ∇T_∞ for heat transfer between flat plates in the Knudsen regime

$$\nabla T_{Kn} = \frac{\nabla T_\infty}{(1+2c_t Kn_2)} = \frac{\nabla T_\infty}{(1+2c_t aKn/H)} \ . \qquad [9]$$

Based on this correction, we use the adjusted force, $(1+2c_tKn_2)F_{th}/(a^2\nabla T_\infty)$, in the presentation of data for Kn > 3.

A small sample of the data published by Li and Davis (1995a,b) are presented herein. Figure 2 shows the effect of the carrier gas on the thermophoretic force for dioctyl phthalate (DOP) droplets. The free-molecule solution of Waldmann is seen to be approached in the limit of large Kn. Figure 3 shows the same asymptotic behavior for glass and polystyrene latex (PSL) spheres and DOP. The properties of the particle are seen to have much smaller effect on the thermophoretic force than the gas properties.

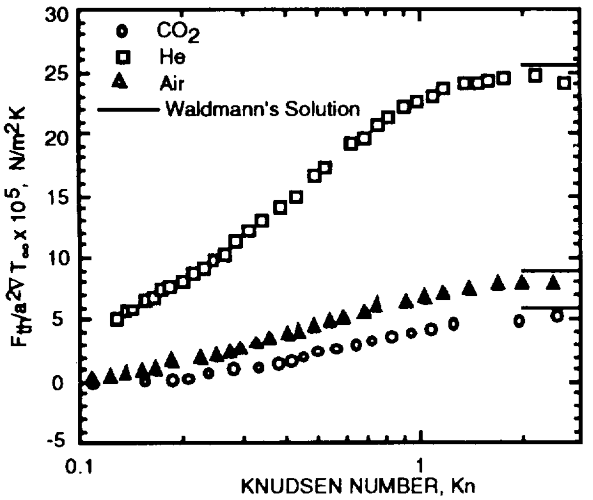

Figure 2. The effect of carrier gas on the thermophoretic force.

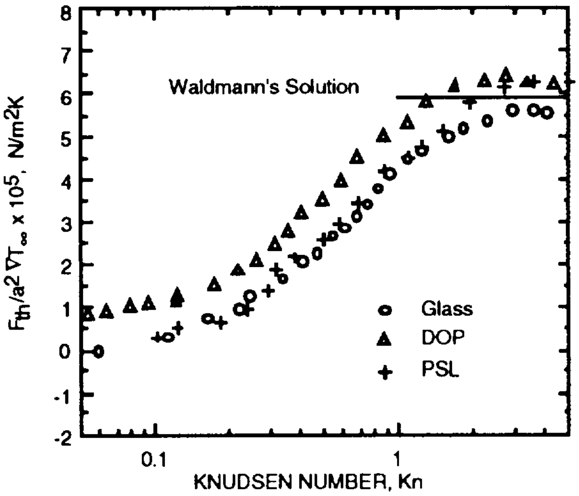

Figure 3. The effect of particle properties on the thermophoretic force.

Figures 4 and 5 compare theoretical and experimental results in air for the four types of particles studied. Loyalka's theory appears to be in reasonable agreement with the data in the Knudsen regime.

Additional work on the measurement of the radiation pressure force is being carried out, and the existing equipment will be modified for diffusiophoresis experiments.

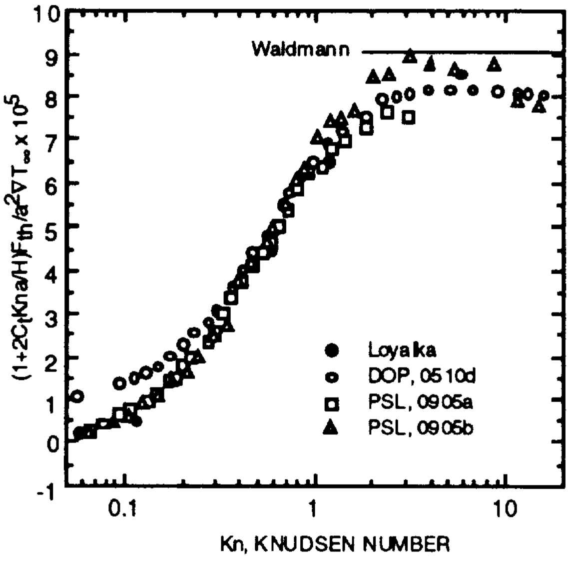

Figure 4. A comparison among the data for DOP and PSL particles and the theories of Waldmann (1959) and Loyalka (1992).

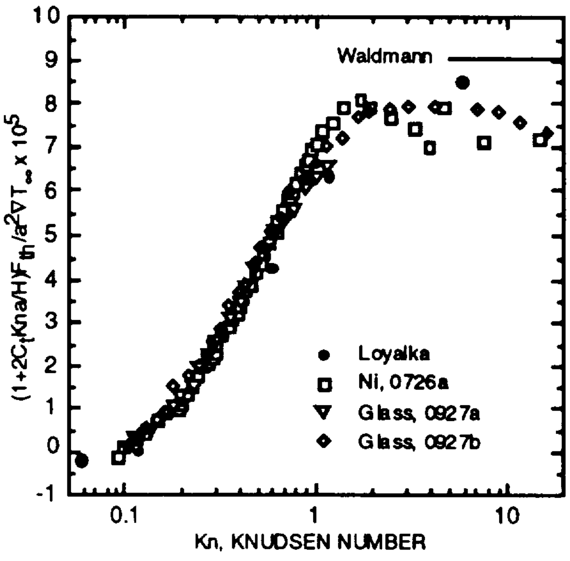

Figure 5. A comparison among the data for nickel and glass spheres and the theories of Waldmann (1959) and Loyalka (1992).

LITERATURE CITED

Bae, G.N., Lee, C.S. and Park, S.O. (1994) *Aerosol Sci. Technol.* **21**, 72-82.

Brock, J.R. (1962) *J. Colloid Sci.* **17**, 768-780.

Davis, E.J., Buehler, M.F. and Ward, T.L. (1990) *Rev. Sci. Instrum.* **61**, 1281-1287.

Davis, E.J. (1992) in *Advances in Chemical Engineering*, Vol. 18, Academic Press, New York, pp. 1-94.

Derjaguin, B.V. and Yalamov, Yu.I. (1972) in *Topics in Current Aerosol Research*, Pergamon Press, Oxford, pp. 1-200.

Devienne, F.M. (1965) in *Advances in Heat Transfer*. Vol. **2**, Academic Press, New York, pp. 272-352.

Dwyer, H.A. (1967) *Phys. Fluids* **10**, 976-984.

Epstein, P.S. (1929) *Z. Physik* **54**, 537-563.

Lee, J.H., Moon, W.S. and Park, S.B. (1996) *Korean J. Chem. Eng.* **13**, 7-14.

Li, W. and Davis, E.J. (1995a) *J. Aerosol Sci.* **26**, 1063-1083.

Li, W. and Davis, E.J.(1995b) *J. Aerosol Sci.* **26**, 1085-1099.

Loyalka, S.K. (1992) *J. Aerosol Sci.* **23**, 291-300.

Maxwell, J.C. (1879) *Phil. Trans. Roy. Soc.*, (see *The Scientific Papers of James Clerk Maxwell*, Vol. 2, Cambridge University Press, pp. 681-712, 1890).

Morse, T.F., Wang, C.Y. and Cipolla, J.W., Jr. (1985) *J. Heat Transfer* **107**, 155-160.

Waldmann, L. (1959) *Z. Naturforsch* **14a**, 589-599.

Waldmann, L. and Schmitt, K.H. (1966) in *Aerosol Science*, C.N. Davies, ed., Academic Press, London, pp. 137-162.

Ye, Y., Pui, D.Y.H., Liu, B.Y.H., Opiolka, S., Blumhorst, S. and Fissan, H. (1991) *J. Aerosol Sci.* **22**, 63-72.