Direct Measurements of Aerosol Diffusion Constants in the Intermediate Knudsen Regime

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The authors have measured the diffusion constants of aerosols whose size compares to the mean free path of the gas in three different aerosols. The experimental diffusion constants do not agree with the kinetic-theory calculations in this intermediate Knudsen regime.

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The diffusion and coagulation of aerosols are of interest in a variety of technical applications[1] as well as in the kinetic theory of gases.[2] An exact description of the diffusion of particles and the calculation of the diffusion constant from the given physical conditions are requirements to understanding aerosol dynamics. Kinetic theory is tested by its ability to predict the diffusion constant. In this Letter, we report light-scattering measurements which indicate a serious error in our ability to calculate the diffusion constant of aerosol particles.

The form of the diffusion constant of a particle suspended in a medium is dependent on the Knudsen number $\mathrm{Kn} = l/r$, where l is the mean free path of the gas molecules and r is the radius of the aerosol. In the hydrodynamic limit where $\mathrm{Kn} \to 0$, the Stokes-Einstein diffusion constant is given by

$$D_{\mathrm{SE}} = kT/f = kT/6\pi\eta r. \tag{1}$$

Here k is Boltzmann's constant, T is the temperature, f is the Stokes drag coefficient, and η is the medium's shear viscosity. This relation is known to hold for particle diffusion in a liquid.

In the kinetic or free molecular limit where $\mathrm{Kn} \to \infty$, the diffusion of particles is less well studied. Theoretically, one expects the Chapman-Enskog diffusion constant to hold:

$$D_{\mathrm{CE}} = (3/8r^2\rho)(kTm/2\pi)^{1/2}, \tag{2}$$

where ρ is the gas density and m is the molecular weight. This relation may also be obtained from the relation $D = kT/f$, and the drag coefficient of Epstein,[3]

$$f = \tfrac{8}{3} r^2 (2\pi kT/m)^{1/2} (1 + \pi\alpha/8), \tag{3}$$

where α is the accommodation coefficient.[2]

In the intermediate Knudsen number regime the diffusion constant has not been calculated directly. The diffusion constant may, however, be obtained in either of two ways. The standard practice[1] has been to use an empirical fit[4] to Millikan's drag coefficient data.[5] The Stokes drag coefficient is corrected by

$$C = 1 + \mathrm{Kn}[A_1 + A_2 \exp(-A_3/\mathrm{Kn})]. \tag{4}$$

Here, $A_1 = 1.255$, $A_2 = 0.4$, and $A_3 = 1.1$. Using $D = kT/f$, one may then obtain D. This is the Cunningham-corrected Stokes-Einstein diffusion constant. A more theoretical approach involves kinetic theory calculations of f[6,7] and then calculating $D = kT/f$. Since the theoretical drag coefficients agree with Millikan's data, these methods are numerically equivalent.

Our experiments to study aerosol diffusion have been performed in two radically different environments. The discrepancy was first noticed during our research on soot nucleation and growth during combustion.[8] The soot-particle diffusion constant in a laminar-slot diffusion flame and a premixed flame was determined as a function of particle size. To corroborate the results from the flame systems, we also generated aerosols of monodisperse polystyrene latex spheres. These three systems, the two burner configurations and the polystyrene microsphere aerosols, involve a wide range of experimental conditions yet lead consistently to the same conclusion, that the diffusion constant is improperly predicted as the Knudsen number becomes nonzero.

The slot burner consisted of two side-by-side rectangular slots, 1×5 cm^2. Slug flows of carbon monoxide and air, each emanating from one slot, mixed via diffusion along the 5-cm-wide interface between the two flows above the slots. Combustion occurred along this interface and soot was formed on the fuel side of the zone. Soot formation resulted from doping the fuel with ~0.01 mole% benzene. A surrounding sheath of slug-flow nitrogen eliminated mixing with atmospheric oxygen.

The premixed burner was 5.5 cm in diameter and was water cooled to stabilize a one-dimensional flame. The flame was further stabilized with a 1-cm-diam steel plate placed roughly 2.5

cm above the burner. The premixed combustion mixture consisted of either methane/oxygen or ethylene/oxygen at equivalence ratios of about 2.

Monodisperse polystyrene suspensions of 0.109- and 0.234-μm-diam microspheres of 10% concentration in water were diluted to approximately $10^{-2}\%$ with methanol. This dilute suspension was then aspirated into a glass tube 1.6 cm in diameter.[9] Flowing dry nitrogen carried this aspirant through a heated region of the tube where the methanol was evaporated leaving individual polystyrene microspheres of known size suspended in the gas. By adjustment of the suspension concentration and liquid droplet size, care was taken to experimentally insure that few dimers of the microspheres formed.

The size of the soot particles was determined by static light-scattering techniques involving the ratio of the light scattered at a finite angle to the extinction at zero angle.[10] Our arrangement used an argon-ion laser ($\lambda = 488$ nm) which was focused into the flame to a diameter of roughly 200 μm. The extinction and scattering measurements at zero angle and 150°, respectively, were each made with fast photomultipliers and photon counting. Narrow-pass filters eliminated the blackbody radiation from the flame for each detector. Calibration of the scattering volume, solid angle, and detector response was made by scattering from pure oxygen gas.

Most of our measurements in the flames were at diameters less than 200 Å. Up to this size soot particles are known to be reasonably spherical.[11] Beyond this size soot growth occurs by chaining of these 200-Å spherical units, but the static light-scattering technique should still yield reasonable values for the effective diameter.

The diffusion constant of the particles was measured by photon-correlation spectroscopy (PCS)[12] in all three systems. The light homodyne detected at finite scattering angle was converted to photopulses for input to a correlator that computed the intensity autocorrelation function of the scattered light. A two-cumulant fit to the approximately exponential correlation function was performed. The first cumulant showed the usual wave-vector squared dependence characteristic of Gaussian diffusion. The diffusion constant was calculated from the first cumulant in the usual manner.

Passage of the particles through the incident laser beam led to the Gaussian-beam transit term[13] (nondiffusional). This beam transit term has width roughly equal to the beam waist divided by the flow velocity, a time of the order of 200 μsec in our experiments. This is considerably longer than most of the correlation times (inverse first cumulant), typically ~10 μsec. The beam transit term is not wave-vector dependent so that it was possible to adjust the scattering angle to insure easy separation of the two signals and accurate determination of the first cumulant, and, hence, the diffusion constant. Experimental reproducibility of the diffusion constant was 1%.

The temperature of the scattering volume in the flame was determined with an optical pyrometer to ± 20 K. The viscosity of the gas was determined from the temperature and gas composition.[14] The mean free path of the gas molecules was calculated from the viscosity.[14]

We present our results for the diffusion constant of the aerosol particles as a function of Knudsen number in Fig. 1. Plotted is the diffusion constant times the particle diameter to allow all the data to be displayed on one graph. Also shown are the theoretical or semiempirical forms discussed above. The soot aerosol data lie in the $15 < \mathrm{Kn} < 100$ regime and all deviated from theory by an order of magnitude. Both flame systems show the same behavior. These data are corroborated by our polystyrene microsphere aerosol data near $\mathrm{Kn} = 1$. Also plotted are data obtained

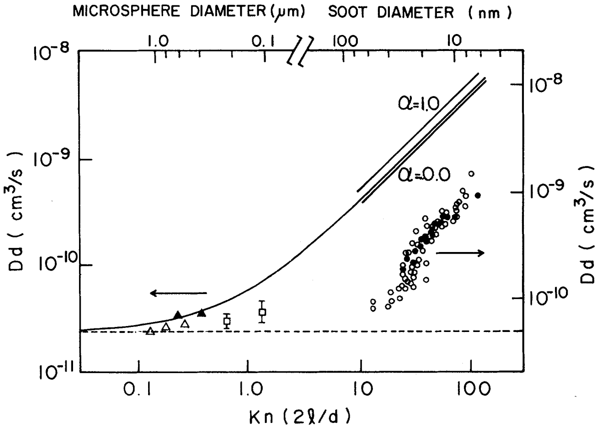

FIG. 1. The product of the measured particle diffusion constant D and the particle diameter d vs the Knudsen number. Open circles, premixed flame; closed circles, diffusion flame; open squares, our polystyrene microsphere aerosols; open triangles, polystyrene microsphere aerosols (Ref. 9); closed triangles, dibutylphthalate aerosols (Ref. 9). Solid line, the Cunningham-corrected Stokes-Einstein formula, equivalent to $\alpha = 0.84$. Dashed line, the uncorrected Stokes-Einstein limit. Note the different ordinates for the two sets of data.

by Hinds and Reist[9] for polystyrene microsphere and dibutylphthalate aerosols. The polystyrene microsphere data show a discrepancy similar to ours, while the dibutylphthalate droplets agree with the theoretical prediction. Thus both our observed discrepancy from theory and the theory itself are corroborated. These data, however, lie near the $\mathrm{Kn}=0$ region where the Stokes-Einstein formula is known to hold, and thus are not expected to show a large deviation from theory.

We have considered a wide range of possible errors in the interpretation of our measurements. Perhaps the largest error in determination of both size and diffusion constant is due to the assumption of a monodisperse size distribution. The soot aerosols are undoubtedly polydisperse. If we consider a general distribution described solely by its first two moments, a distribution width to mean radius ratio of 0.5 would shift our data upward and *parallel* to the theoretical curve to the $30<\mathrm{Kn}<180$ region. In fact any reasonable polydispersity causes such a parallel shift and cannot improve the comparison of theory to experiment.

Another source of error is the uncertainty in the refractive index of soot. Although we used a value of $n=1.56-i0.57$,[15] there are a number of other values available in the literature. The uncertainties in n lead to, at most, an uncertainty in particle diameter of 20%, which is within the scatter of our data and is nowhere near large enough to account for the discrepancy.

We have also considered phoretic forces. Drift due to a force would cause a Doppler shift in the scattered light. A dispersion of forces across the scattering volume is, therefore, necessary to broaden the diffusional profile and affect the measured diffusion constant. Since the forces themselves depend upon gradients, this broadening is a second-order effect. Furthermore, the measured diffusion constant would tend to be too big, not too small (see Fig. 1).

Despite these arguments we attempted to distinguish any effect the phoretic forces might have experimentally. Thermophoresis should be large in the diffusion flame because of the large transverse temperature gradients in the combustion zone. On the other hand, the premixed flame has a very flat radial temperature profile and an axial gradient that is less than 1% as large as that in the diffusion flame. That both burners yielded equivalent data implies that thermophoretic forces are insignificant. There are no thermophoretic effects in the polystyrene microsphere aerosol. Similar arguments can be made concerning diffusiophoretic effects. Photophoretic effects were checked by varying the input laser beam power by a factor of 10. No effect on the results was seen.

Turbulence would also tend to broaden the scattered-light spectrum and thus make the diffusion constant look bigger, not smaller, as observed. All our systems have been designed to ensure laminar flow.

The effect of charge on the aerosols must be considered. It is known that in dilute aqueous solutions the first effect of Coulombic interaction is to increase the diffusion constant,[16] opposite to the discrepancy we report. The corroboration of three different aerosol systems also suggests that charge effects are not important. The fraction of soot particles with charge varies substantially along the axis of the premixed flame,[11] and might be expected to vary likewise through the diffusion flame. Our measurements, taken throughout the sooting regions of both flames, show a consistent deviation from the theory. If charge were affecting the diffusion of the soot particles, we would see a slope of the diffusion constant versus Kn different from that predicted by kinetic theory.

Recently Kim and Fedele[17] have studied single-particle diffusion in a gas. They found a deviation from Millikan's law of fall, which is the empirical basis of the Cunningham term, Eq. (4), used to describe drag and diffusion in the intermediate Knudsen regime. They interpreted their experiment, however, to show a deviation at small Knudsen numbers, the law of fall working better as the Knudsen number increases, a behavior opposite to that which we have observed.

In conclusion, we have measured the diffusion constant of a variety of submicron aerosols and the value of the diffusion constant predicted by kinetic theory or the Cunningham-corrected Stokes-Einstein formula is too large by as much as a factor of 10. Various sources of error or spurious effects have been considered but cannot explain this discrepancy.

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