Measurements of the Diffusion Coefficient for Soot Particles in Flames

W. L. Flower
Sandia National Laboratories, Livermore, California 94550
(Received 26 August 1983)

Diffusion coefficients for soot particles were measured in a flame with use of a dynamic–light-scattering technique. Experimental measurements for particle Knudsen numbers in the range from 10 to 75 are in good agreement with the results of kinetic-theory calculations.

PACS numbers: 51.20.+d, 05.40.+j, 82.70.Rr

An understanding of the diffusion of small particles is essential to a number of applications related to the mechanics of aerosol behavior, including coagulation theory and the design of gas-cleaning and aerosol-sampling systems.[1] In recent years, dynamic–light-scattering techniques,[2] which rely on measurements of the spectral broadening of scattered light due to the motion of the scattering particles, have been used to determine particle size in a variety of environments, including biological[3] and combustion[4-6] systems. The accuracy of such measurements relies on a knowledge of the dependence of the particle diffusion coefficient on the size of the particle. At small Knudsen number N_{Kn} (the ratio of the mean free path of the gas molecules to the particle radius), the diffusion coefficient D for spherical particles of diameter d is given by the Stokes-Einstein expression,[1]

$$D_{\mathrm{S\text{-}E}} = kT/3\mu\pi d. \quad (1)$$

Here μ is the viscosity of the gas. For large N_{Kn}, the diffusion coefficient is obtained from kinetic theory[1]:

$$D_{\mathrm{kin}} = 3kTl/2\mu\pi(1+\pi\alpha/8)d^2, \quad (2)$$

where l is the mean free path of the gas molecules, and α is the accommodation coefficient. At intermediate values of N_{Kn}, the diffusion coefficient is given by the Cunningham correction to the Stokes-Einstein relation,[7]

$$D_{\mathrm{Cun}} = D_{\mathrm{S\text{-}E}}\{1 + N_{\mathrm{Kn}}[A + B\exp(-C/N_{\mathrm{Kn}})]\}, \quad (3)$$

where the constants A, B, and C are obtained from an empirical fit to Millikan's drag-coefficient data.[8] Equation (3) approaches the Stokes-Einstein relation as N_{Kn} goes to zero and approaches the kinetic-theory result as the Knudsen number goes to infinity.

Since the Knudsen number for soot particles in flames is typically of order unity or larger, the latter two expressions for the diffusion coefficient have commonly been used in such applications.[4,6] However, a recent study of soot-particle diffusion using dynamic–light-scattering techniques[9] has cast doubt on the validity of the Cunningham relation in this regime. Soot diffusion coefficients measured in that study using photon-correlation spectroscopy are about an order of magnitude smaller than calculated from the Cunningham expression evaluated with soot diameters determined from static-light-scattering techniques. Since the Cunningham diffusion coefficient is within a few percent of the kinetic-theory value for the Knudsen numbers at which soot measurements were made, the diffusion coefficients reported in Ref. 9 are in fundamental disagreement with the predictions of kinetic theory.

Experiments conducted in this laboratory to study the growth of soot particles in flames also provide information regarding the diffusion constants for soot particles. Soot volume fractions inferred from static–light-scattering measurements have been found to be in good agreement with volume fractions based on dynamic–light-scattering measurements,[4] implying that the Cunningham expression (which was used in the analysis of the dynamic–light-scattering data) satisfactorily predicts particle diffusion coefficients for the conditions of this study. Since only a few direct comparisons between the different measurement techniques were made, further experiments have recently been conducted to look for evidence of the surprisingly slow particle diffusion reported in Ref. 9. This Letter reports the findings of a study in which techniques similar to those of Ref. 9 were used to measure soot diffusion coefficients directly, but with much different results: The diffusion coefficients presented here are 6–7 times larger than reported in Ref. 9 and are in reasonable agreement with the predictions of kinetic theory.

The burner used in the present study and the apparatus used for dynamic–light-scattering measurements have been described in detail previously.[4] Basically, the flame used here was a

premixed methane/oxygen flat flame supported on a cooled porous-plug burner (6.0 cm diam) and surrounded by a shroud flow of nitrogen. This arrangement produced a steady, nearly one-dimensional flame. Measurements were made at positions from 5 to 15 mm above the burner surface for fuel/oxidizer equivalence ratios between 2.2 and 2.8.

Soot diffusion coefficients were determined from the spectral broadening of scattered laser light. The beam from the argon-ion laser (514.5 nm) used as the probe passed through the flame gases in a plane parallel to the burner surface. Light scattered at 5° from the forward direction was collected by a detection system consisting of a 10-cm-focal-length lens, an adjustable vertical slit at the image plane of the probe volume, a narrow-bandpass interference filter, and a photomultiplier tube. The photomultiplier-tube output was amplified, and the photocurrent power spectrum was measured with use of a fast-Fourier-transform spectrum analyzer.

The photocurrent power spectrum which results from scattering from a collection of particles consists of the sum of three terms: a delta function at zero frequency corresponding to the dc photocurrent; the contribution of shot noise, a constant with frequency; and a Lorentzian function of frequency given by[2]

$$P(\omega) = \frac{I^2K^2D/\pi}{(2K^2D)^2+\omega^2}. \quad (4)$$

Here I is the intensity of scattered light, and K is the magnitude of the scattering wave vector. The half-width of the Lorentzian portion of the power spectrum, $\Delta\omega = 2K^2D$, is proportional to the particle diffusion coefficient. It is assumed here that the diffusion coefficient is the same for all particles (i.e., the particles are of uniform size) and that the collection of particles has no mean translational motion.

The uncertainty resulting from the first assumption is not accurately known since, although a distribution of particle sizes is commonly believed to be present in sooting flames, the exact form of the particle size distribution is not well characterized. The assumption of zero mean translational motion is valid in flowing systems if the Lorentzian half-width is much larger than the inverse of the particle transit time through the laser beam, as was the case in this study.

A typical photocurrent power spectrum is shown in Fig. 1. The irregular solid curve represents measurements of power spectral density obtained

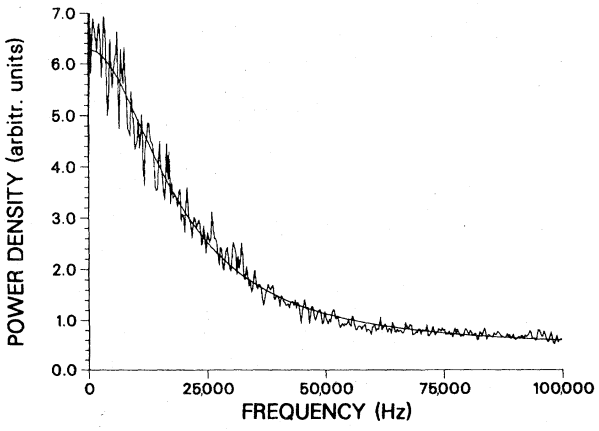

FIG. 1. Measured homodyne power spectrum (irregular solid curve) and the Lorentzian profile plus constant base line which best fits the measured spectrum (smooth curve). Measurements were made 7.5 mm above the burner surface in a methane/oxygen flame at an equivalence ratio of 2.4.

in an averaging period of 25 sec. The smooth curve in Fig. 1 was obtained by a least-squares fit of a Lorentzian profile plus a constant base-line term to the measured power spectrum. Particle diffusion coefficients were determined from the Lorentzian widths of the best-fit spectra. The particle diameter d_{dls} corresponding to the dynamic-light-scattering measurement of the diffusion coefficient was determined from D by the Cunningham relation, Eq. (3).

Independent measurements of the sizes of the soot particles were obtained using standard static-light-scattering techniques. The scattering intensity I_{scat} is proportional to the product of the particle number density N and the scattering cross section σ_{scat}, a function[10] of the particle diameter, the scattering angle θ (90° here), and the particle complex refractive index m:

$$I_{\mathrm{scat}} = C\sigma_{\mathrm{scat}}(d,\theta,m)N. \quad (5)$$

The calibration constant C was determined by measurement of scattering from flowing nitrogen. Scattering from flowing helium, which has a much smaller Rayleigh-scattering cross section, was measured to ensure that no stray light was detected from other sources.

The transmission of laser light through the soot-laden gases was measured simultaneously by means of a silicon photodiode. The ratio of the transmitted laser intensity to the initial intensity for propagation through a collection of particles of uniform size and number density is

given by[10]

$$\tau = I/I_0 = \exp(-\sigma_{ext} NL), \quad (6)$$

where $\sigma_{ext} = \sigma_{ext}(d,m)$ is the extinction cross section. The optical path length L was determined by traversing the burner in the direction along the laser beam and measuring the variation in the intensity of scattered light at 90°.

The measurements of the transverse variation of scattering, along with measurements of the transverse variation of temperature, also provide an indication of the degree of uniformity of the flame properties in a horizontal plane. Such measurements showed that, at a fixed vertical position, temperature and scattering were constant within a few percent over the central 80% of the diameter. At the edge of the flame, temperature decreased from its flame value to ambient temperature, while scattering increased severalfold and then fell sharply to zero. The increase in scattering at the flame edge probably resulted from an increase in the particle number density as the soot-laden gases were cooled, a physical model which is consistent with the measured variation of temperature.

For the case where N and σ_{ext} are assumed constant in a horizontal plane, the ratio of the scattering cross section to the extinction cross section provides a relation between particle size and known or measured quantities:

$$\frac{\sigma_{scat}(d,\theta,m)}{\sigma_{ext}(d,m)} = -\frac{LI_{scat}}{C \ln \tau}. \quad (7)$$

The soot particle diameter d_{s-e} corresponding to the measured scattering-to-extinction ratio was determined by solving Eq. (7) for d, evaluating the extinction and scattering cross sections with the full Mie theory for scattering from spherical particles[10] with refractive index $m = 1.57 - i0.56$.[11]

The effect of horizontal variation of N on the measurement of particle size was estimated by using the scattering measurements and Eq. (5) to solve for N in terms of $\sigma_{scat}(d,\theta,m)$, which was assumed constant in this case. The measured variation of N was then substituted into the differential equation describing extinction by particles,[4] which was used to obtain an alternative relation between σ_{ext} and σ_{scat}. This expression was then solved for the particle diameter. This procedure resulted in corrected values of d_{s-e} which were 5%–15% larger (depending on the vertical position) than obtained when the flame was assumed to be one dimensional. A similar procedure showed that correction factors closer to unity were obtained if the transverse variation in scattering was assumed to result from variations in the particle diameter rather than number density.

The diffusion coefficients measured in the present study are compared in Fig. 2 with the soot measurements of Ref. 9 and the predictions of the Cunningham expression. The Cunningham diffusion coefficient was calculated from Eq. (3) on the assumption that the gas temperature was the same as the temperature of the soot particles, which was determined from simultaneous measurements of the emission and absorption of light by the particles.[4] The molecular mean free path and gas viscosity were calculated from the measured temperature.[12,13] Plotted in Fig. 2 is the product of the diffusion coefficient and the particle diameter as a function of Knudsen number. The ordinate for the experimental results is the product of two different measurements, the dynamic–light-scattering measurement of D and the static–light-scattering measurement of d. A least-squares fit to the values of Dd measured in this study is between 0.68 and 0.88 times the value predicted by the Cunningham expression, as compared to the data of Ref. 9, which are about 0.1 times the Cunningham prediction for the same values of N_{Kn}. Correction of the fit to the data for the effect of the transverse variation in N on the measurement of d_{s-e} results in values of Dd between 0.88 and 0.95 times the value predicted by the Cunningham expression.

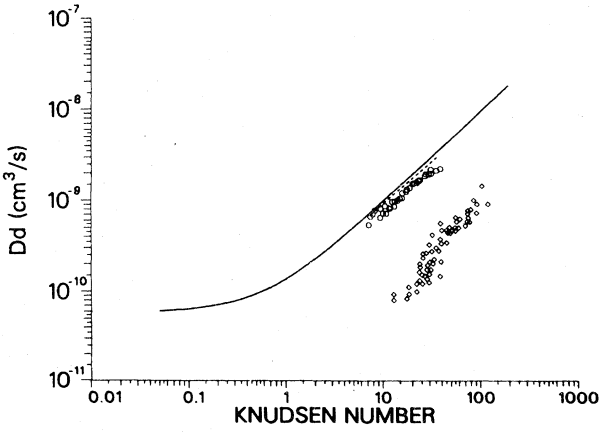

FIG. 2. Plot of the product of particle diameter d and particle diffusion coefficient D as a function of the Knudsen number. Solid curve, theoretical value obtained using the Cunningham expression; circles, measurements, this study; dashed line, fit to the data of this study after correction for two-dimensional effects; diamonds, measurements, King *et al.* (Ref. 9).

The difference between the measured and theoretical values of Dd cannot be attributed entirely to a discrepancy in D. Since the diffusion coefficient is inversely proportional to the square of the particle diameter in the free-molecular-flow limit, the experimental value of Dd is proportional to $d_{s-e}/d_{\mathrm{dls}}{}^2$. The theoretical value of Dd is proportional to $1/d_{s-e}$, and, hence, the ratio of the experimental value of Dd to the theoretical value is proportional to $(d_{s-e}/d_{\mathrm{dls}})^2$. Thus, an alternative way of viewing the present measurements is that the corrected particle size determined from static-light-scattering measurements is 0.94 to 0.98 times as large as d_{dls}. This excellent agreement between the two size-measurement techniques emphasizes the fact that the results displayed no significant departure from kinetic theory; however, the closeness of the agreement must be considered in part fortuitous in view of the uncertainties in the particle size distribution, shape, and refractive index.

In summary, the fundamental disagreement reported in Ref. 9 between measured soot-particle diffusion coefficients and the predictions of kinetic theory was not observed in the present study. On the contrary, the measurements reported here provide direct evidence supporting the validity of the kinetic-theory expression for soot-particle diffusion coefficients in flames.

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences.

[1]N. A. Fuchs, *The Mechanics of Aerosols* (Pergamon, London, 1964).

[2]H. Z. Cummins and H. L. Swinney, *Progress in Optics VIII*, edited by E. Wolf (North-Holland, Amsterdam, 1970), p. 135.

[3]P. Schurtenberger, N. Mazer, and W. Kaenzig, J. Phys. Chem. 87, 308 (1983).

[4]W. L. Flower, Combust. Sci. Technol. 33, 17 (1983).

[5]S. S. Penner, J. M. Bernard, and T. Jerskey, Acta Astronaut. 3, 93 (1976).

[6]G. B. King, C. M. Sorensen, T. W. Lester, and J. F. Merklin, Appl. Opt. 21, 976 (1982).

[7]E. Cunningham, Proc. Roy. Soc. London 83, 359 (1910).

[8]C. N. Davies, Proc. Phys. Soc. London 57, 259 (1945).

[9]G. B. King, C. M. Sorensen, T. W. Lester, and J. F. Merklin, Phys. Rev. Lett. 50, 1125 (1983).

[10]M. Kerker, *The Scattering of Light and other Electromagnetic Radiation* (Academic, New York, 1969).

[11]W. H. Dalzell and A. F. Sarofim, J. Heat Transfer 91, 100 (1969).

[12]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[13]E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).