Size- and Structure-Insensitivity of the Thermophoretic Transport of Aggregated "Soot" Particles in Gases

D. E. ROSNER [a] , D. W. MACKOWSKI [a] & P. GARCIA-YBARRA [a]

[a] Department of Chemical Engineering. High Temperature Chemical Reaction Engineering Laboratory, Yale University, New Haven, CT, 06520-2159, U.S.A
Version of record first published: 06 Apr 2007.

PLEASE SCROLL DOWN FOR ARTICLE

Size- and Structure-Insensitivity of the Thermophoretic Transport of Aggregated "Soot" Particles in Gases

D. E. ROSNER, D. W. MACKOWSKI and P. GARCIA-YBARRA

Yale University, Department of Chemical Engineering, High Temperature Chemical Reaction Engineering Laboratory, New Haven, CT 06520-2159, U.S.A.

Abstract—There is now convincing theoretical and experimental evidence, assembled and discussed here, for the remarkable insensitivity of the orientation-averaged *thermophoretic* properties of aggregated particles to aggregate size and structure (morphology), as well as the nature of gas/surface scattering. Indeed, theoretical consideration of straight chains, and uniformly "packed" quasi-spherical agglomerates, as well as recent experimental data on soot aggregate transport in/from laminar flames at atmospheric pressure, indicates that the orientation-averaged thermophoretic diffusivity, $\langle \alpha_T D \rangle_N$, of an aggregate containing N primary particles is usually within about 8% of the $(\alpha_T D)_1$-value for a single "primary" sphere in the free-molecule regime and within about 21% in the continuum limit. Among other things, this implies that, especially in the free-molecule regime, thermophoretically-dominated transport rates can be adequately predicted *without* a detailed knowledge of the size and morphology (-distribution) of the aggregated particles or the nature of gas/particle surface scattering, which is definitely *not* the case for particle transport by Brownian diffusion or inertial drift (see, *e.g.*, Rosner, 1991). This result also implies that thermophoretic particle sampling from "low pressure" flames (Dobbins and Megaridis, 1987) does not itself introduce a significant bias in the relative populations of various sampled aggregate sizes and morphologies. As a corollary, local gas temperature and soot volume fraction estimates based on mass transfer rates- or thermocouple response-methods (Eisner and Rosner, 1985, 1986) will be negligibly influenced by the inevitably uncertain sizes and morphologies of the prevailing soot agglomerates. Since the optical properties (*e.g.*, effective cross-sections for light-scattering and extinction) of soot aggregates are now known to be size- and structure-*sensitive* (Mackowski, 1987, 1988, Dobbins, Santoro, and Semerjian, 1991, Dobbins and Megaridis, 1991)) we anticipate that the drag *vs.* thermal force "compensation" effects that produce $\langle \alpha_T D \rangle$-values *insensitive* to aggregate *size* (N), *and structure, and the nature of gas molecule/surface scattering* will find important R & D applications for many systems in which agglomeration occurs. It is also concluded that thermophoretic means would *not* be useful to rapidly separate various asymmetric particle morphologies unless orientation-averaging is suppressed, perhaps using external fields (**E, B**).

Key words: Soot, aggregated particles, mass transport, thermophoresis, agglomerates; Brownian diffusion.

1 INTRODUCTION

In many technologies, including those involving organic- and inorganic "soot" production in combustors, fine suspended particles are formed by chemical reactions and/or the physical nucleation of vapors, yet coalescence rates are unable to compete with the inevitable coagulation rates, leading to highly "aggregated" particles (see, *e.g.*, Ulrich *et al.*, 1977, 1982, Megaridis and Dobbins, 1990). These aggregates are comprised of much smaller "primary" particles, frequently themselves highly spherical and remarkably "monodispersed" (narrow-spread in primary particle diameters). The simultaneous presence of many aggregate sizes and morphologies evidently complicates the task of predicting the evolution and transport of such "particles", including their deposition or capture. It also complicates the research task of measuring their numbers and characteristics, especially *in situ* using optical techniques (see, *e.g.*, Dobbins, Santoro, and Semerjian, 1991). The purpose of this paper is to point out that whereas the Brownian diffusion-, inertial-and/or optical properties of such aggregates are indeed quite sensitive to aggregate size and morphology, the *thermophoretic properties* of such particles (*i.e.*, their migration behavior in reponse to an

imposed temperature gradient in the gas phase) are remarkably *insensitive* to aggregate size and morphology, with rather important research and technological implications briefly discussed below.

The situation will be seen to be particularly striking in the free-molecule limit where, for example, it is known that an aggregate containing 100 primary particles would necessarily have an orientation-averaged Brownian diffusion coefficient $\langle D_N \rangle$ less than 4.6% ($=(100)^{-2/3}$) that of the primary sphere, and $\langle D_N \rangle$ could itself easily differ by nearly an order of magnitude depending upon the aggregate *morphology* (*e.g.*, linear?, quasi-spherical?, fractal-like?,...) (see, *e.g.*, Rosner, 1990, Rosner *et al.*, 1991). In contrast, we show below that the orientation-averaged thermophoretic diffusivity $\langle \alpha_T D \rangle_N$ defined by the drift velocity expression:

$$\mathbf{V}_T = \langle \alpha_T D \rangle_N \cdot (-\mathbf{grad}\ T_g)/T_g, \tag{1}$$

is within about 8% of the value for an isolated "primary" sphere in the same gaseous environment for all aggregate sizes (designated *via* the integer index N for the number of primary particles in the linear aggregate). The underlying reason for this will be seen to reside in the similar way in which both the net *thermal force* and the aggregate *drag* depend upon aggregate size and morphology. This approximate "cancellation" of size- and morphology-effects also occurs in the near-continuum (high-pressure-) limit, but to a somewhat smaller extent. In the discussion below we consider both Knudsen number limits ($Kn \ll 1$ and $Kn \gg 1$), bearing in mind that future research will be necessary to better characterize the transport behavior of such aggregates in the more difficult "transition" regime (intermediate Knudsen numbers).

2   EVIDENCE FOR THE SIZE- AND STRUCTURE-INSENSITIVITY OF $\langle \alpha_T D \rangle_N$

While admittedly incomplete, there is already convincing evidence, both theoretical and experimental, for the insensitivity of $\langle \alpha_T D \rangle_N$ to both aggregate size, N, and morphology, especially in the free-molecule limit and (to a somewhat smaller extent) in the near-continuum limit. The evidence is briefly reviewed in each of the sub-sections below. For additional details the reader is directed to the specific references cited (Section 5).

2.1   Chain-like (*Elongated*) Particles in the Free-Molecule Limit

In free-molecule flow the insensitivity of particle thermophoretic transport to particle structure can be considered separately from two different viewpoints: *size* and *shape* effects. First, because thermal as well as resistance forces are both proportional to the particle cross-section, this factor cancels and the induced thermophoretic velocity does not depend on particle *size* (*i.e.*, mean cross-section). Second, although non-spherical -particles exhibit differential cross-sections depending on each particular orientation, these shape effects almost cancel out when averaged over all possible orientations attained by the non-spherical particles due to Brownian rotation. As a consequence, the orientation-averaged thermophoretic velocity is only weakly dependent on particle morphology due to these shape effects. Detailed calculations have been carried out recently for sphero-cylindrical particles by García-Ybarra and Rosner (1989). Their results concerning the particle aspect-ratio dependence are summarized and discussed briefly in the following.

Focusing attention only in the resistance and thermal forces acting on a sphero-cylindrical particle (*i.e.*, a cylinder of length L and radius R with hemispherical caps on both ends) moving with velocity $\mathbf{V}$ relative to a carrier gas subjected to a temperature gradient **grad** T_g, the total force on the particle can be written:

$$\mathbf{F} = -N_g \pi R^2 \sqrt{2\pi m k_B T_g} \cdot (\mathscr{R} \cdot \mathbf{V} + \tfrac{3}{4} v \mathscr{T} \cdot \mathbf{grad}\ln T_g), \tag{2}$$

where N_g, m and v are the local molecular number density, the molecular mass and the kinematic viscosity of the carrier gas, respectively, k_B is the Boltzmann constant and T_g the common absolute temperature. The dimensionless thermal force matrix $\mathscr{T}$ and the resistance matrix $\mathscr{R}$, when referred to the principal symmetry axis of the sphero-cylinder, are found to be

$$\mathscr{T}_{11} = \mathscr{T}_{22} = \tfrac{8}{3} + \frac{2L}{R}\left(1 - \frac{a}{4}\right), \tag{3}$$

$$\mathscr{T}_{33} = \tfrac{8}{3} + \frac{L}{R}a, \tag{4}$$

$$\mathscr{R}_{11} = \mathscr{R}_{22} = \mathscr{T}_{11} + a\frac{\pi}{3}\left(1 + \frac{3L}{4R}\right), \tag{5}$$

$$\mathscr{R}_{33} = \mathscr{T}_{33} + a\frac{\pi}{3}, \tag{6}$$

$$\mathscr{R}_{ij} = \mathscr{T}_{ij} = 0, \quad (i \neq j). \tag{7}$$

Here a is the *diffuse reflection fraction* of the impinging molecules. The subscript 3 refers to the coordinate axis along the sphero-cylinder and the subscripts 1, 2 to the other orthogonal axes on the normal plane. The quasi-steady thermophoretic velocity of the particle is obtained by equating the components of $\mathbf{F}$ to zero in Eq. (2). Thus,

$$\mathbf{V}_T = -\tfrac{3}{4}v\,(\mathscr{R}^{-1} \cdot \mathscr{T}) \cdot \mathbf{grad}\ln T_g, \tag{8}$$

which shows that $\mathbf{V}_T$ does not depend on particle cross-section (particle size) and that, in general, $\mathbf{V}_T$ and **grad** T_g will have different directions. By averaging over all particle orientations (assuming equiprobability in the absence of a net torque) we obtain

$$\langle\mathbf{V}_T\rangle = -(\tfrac{3}{4}v)\tfrac{1}{3} \cdot \mathrm{Trace}(\mathscr{R}^{-1} \cdot \mathscr{T})\,\mathbf{grad}\ln T_g \tag{9}$$

Note that the proportionality factor can be identified with the orientation-averaged product $\langle \alpha_T D\rangle$ of the binary thermal diffusion factor α_T and the Brownian diffusion coefficient D, by analogy with the equivalent result of kinetic theory of gases for a quasi-Lorentzian gas of spheres (Mason, 1957; Waldmann and Schmitt, 1966) where

$$[\alpha_T D]_{sph} = \frac{3v}{4(1 + a\pi/8)}, \tag{10}$$

Then, from Eq. (9) we can write

$$\frac{\langle\alpha_T D\rangle}{[\alpha_T D]_{sph}} = \frac{1 + a\pi/8}{3} \cdot \left(\frac{2\mathscr{T}_{11}}{\mathscr{R}_{11}} + \frac{\mathscr{T}_{33}}{\mathscr{R}_{33}}\right). \tag{11}$$
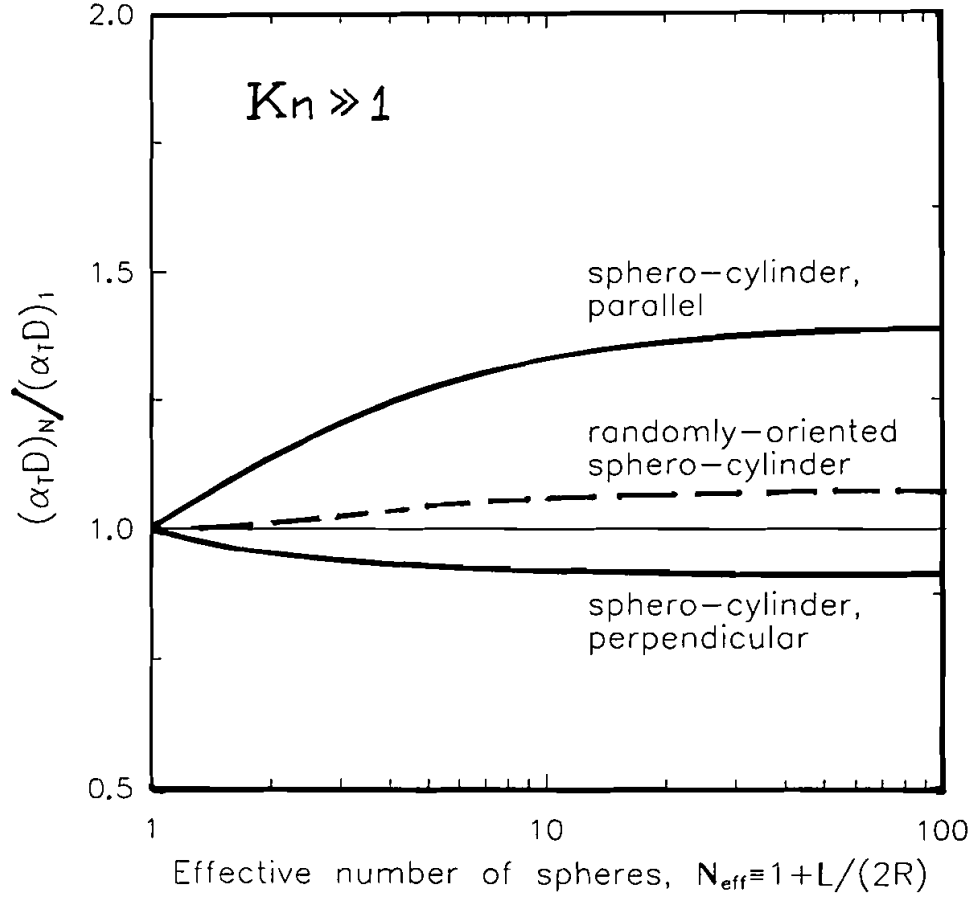
FIGURE 1   Predicted thermophoretic properties of straight chain-like particles in the free-molecule ($Kn \gg 1$) limit, with diffuse reflection ($a = 1$) at the gas/particle interface (after Garcia-Ybarra and Rosner, 1989).

Through the L/R dependence of the diagonal components of $\mathscr{R}$ and $\mathscr{T}$ this relation summarizes the shape (aspect-ratio) effects. Remarkably enough, because of the appearance of $\mathscr{T}_{ii}/\mathscr{R}_{ii}$-ratios, numerical computations show that over the entire range of L/R values, the maximum departures from the spherical value correspond to $a = 1$ and are less than 8%. Figure 1 displays our results for the normalized values of $\langle \alpha_T D \rangle$ as a function of the modified aspect ratio parameter $N_{\text{eff}} = 1 + (L/2R)$. Also shown are the values of this thermophoretic factor for frozen Brownian rotation when **grad** T_g is directed along the sphero-cylinder, $(\alpha_T D)_{par} = (3/4)v\mathscr{T}_{33}/\mathscr{R}_{33}$, and when it is directed perpendicularly, $(\alpha_T D)_{per} = (3/4)v\mathscr{T}_{11}/\mathscr{R}_{11}$.

By way of contrast, for the case of the Brownian diffusion coefficient, we have

$$\langle D \rangle = k_B T \langle b \rangle, \tag{12}$$

where the orientation-averaged mobility $\langle b \rangle$ is obtained exclusively from the inverse resistance matrix $\mathscr{R}^{-1}$ as

$$\langle b \rangle = (N_g \pi R^2 \sqrt{2\pi m k_B T})^{-1} \cdot \tfrac{1}{3} \text{Trace}(\mathscr{R}^{-1}) \tag{13}$$

Equations (12) and (13) show the strong inverse proportional dependence of $\langle D \rangle$ on mean particle cross section for a sphero-cylinder.

Denoting the mobility of a sphere of radius R as:

$$b_{sph} = (N_g \pi R^2 \sqrt{2\pi m k_B T})^{-1} \cdot \frac{3}{8 + a\pi}, \tag{14}$$

then:

$$D_{sph} = k_B T b_{sph}, \tag{15}$$

and the corresponding orientation-averaged Brownian diffusion coefficient, Eq. (12) can be written

$$\frac{\langle D \rangle}{D_{sph}} = \frac{8 + a\pi}{9} \left(\frac{2}{\mathscr{R}_{11}} + \frac{1}{\mathscr{R}_{33}} \right). \tag{16}$$

Introducing the abovementioned values of $\mathscr{R}_{11}$ and $\mathscr{R}_{33}$ we therefore obtain*

$$\frac{\langle D \rangle}{D_{sph}} = \left\{ 1 + \frac{L}{2R} \cdot \frac{1 - \frac{6a}{8 + a\pi} \left[1 - \frac{3L}{2R} \cdot \left(\frac{1}{2} - \frac{a}{8 + a\pi} \right) \right]}{1 + \frac{L}{2R} \cdot \left(\frac{1}{2} + \frac{3a}{8 + a\pi} \right)} \right\}^{-1} \tag{17}$$

Numerical estimates from Eq (17) show that in practical situations (with $a = 1$) $\langle D \rangle$ for a sphero-cylinder of length L falls off rapidly as L/R increases (because of the $(\mathscr{R}_{ii})^{-1}$ terms).†

2.2 Particle Chains and Quasi-Spherical Aggregates in the Near-Continuum Limit

In the near-continuum flow regime (Kn (based, say, on the inverse of the maximum load surface curvature) $\ll 1$) the thermophoretic motion of a particle of arbitrary shape can, in principle, be obtained through solution of the diffusion (conduction) equation for the fluid and particle temperature, and the creeping flow equations for the fluid velocity (see, e.g., Happel and Brenner, 1965, and Kim and Karrila, 1990). The boundary conditions for these equations must account for the temperature and tangential velocity "jumps" at the surface of the particle, due to the inevitable presence of a Knudsen sublayer, and the thermal "creep" slip flow at the surface arising from a local tangential temperature gradient in the gas (see, e.g., Rosner, 1989a).

For certain particle surfaces conforming to an orthogonal coordinate system, exact solution of the equations is possible. For example, Leong (1984) investigated the

---

*This expression corrects misprints appearing in the corresponding equation of García-Ybarra and Rosner (1989).

†It is interesting to note that this fall off is such that the product of $\langle D \rangle$ and the orientation-averaged cross section, $\pi R^2[1 + (L/2R)]$, remains nearly constant (to within about 25%). However, this approximate dependence on orientation-averaged cross-section fails for small values of a. In fact, for $a = 0$ the cylindrical part would move freely along its axis of revolution and, if, in addition, $L/R \rightarrow \infty$, this is the only allowed direction of motion. Yet, the diffusion coefficient does not diverge (nor vanish) but reaches a constant value equal to one third of D_{sph} due to the hemispherical caps at the cylinder ends.

thermophoretic behavior of prolate and oblate spheroids in the continuum ($Kn = 0$) limit and aligned parallel to the temperature gradient. Williams (1987) utilized the bispherical coordinate system to formulate the thermophoretic behavior of a pair of identical spheres. An alternative solution of the two-sphere aggregate problem was obtained by Mackowski (1990), through use of a coupled spherical harmonic technique. The general conclusions of these investigations is that the thermophoretic velocity of an elongated particle, when compared to that of a sphere, is greater when the temperature gradient is parallel to the long axis of the particle, and less when the gradient is perpendicular to this axis. Orientation averaging thus produces an "effective" thermophoretic diffusivity that is not significantly different than the volume-equivalent sphere thermophoretic diffusivity.

Determination of the thermophoretic behavior of more complicated particles than spheroids or binary aggregates would provide more insight into the structure sensitivity of the thermophoretic diffusivity. A particular type of particle that occurs frequently in nature, yet allows for a tractable mathematical analysis, is an aggregate of several spheres. Solution of the conduction and creeping flow equations for such structures can be accomplished using an extension of the coupled spherical harmonics solution. Details of the formulation will be published in a separate paper (Mackowski, 1991), and are simply outlined here.

The analysis is based on the fact that solutions in the spherical coordinate system to the conduction and creeping flow equations can be expressed as infinite series involving spherical harmonics. Specifically, the fluid temperature and velocity fields that satisfy these respective equations and vanish at infinite distance from the origin can be written

$$T_f = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} d_{mn} u_{mn}\{r, \theta, \phi\}, \tag{18}$$

$$\mathbf{v} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ a_{mn} \nabla u_{mn}\{r, \theta, \phi\} \right.$$

$$+ b_{mn} \left(\frac{1}{n} r u_{mn}\{r, \theta, \phi\} - \frac{n-2}{2n(2n-1)} \nabla [r^2 u_{mn}\{r, \theta, \phi\}] \right)$$

$$\left. + c_{mn} \nabla \times [r u_{mn}\{r, \theta, \phi\}] \right\}, \tag{19}$$

where $u_{mn}\{r, \theta, \phi\}$ denotes the solid spherical harmonic:

$$u_{mn}\{r, \theta, \phi\} = r^{-(n+1)} P_n^m \{\cos \theta\} e^{im\phi}. \tag{20}$$

The expansion coefficients a_{mn}, b_{mn}, c_{mn} and d_{mn} are specified upon application of the boundary conditions to the solutions.

The governing differential equations and boundary conditions are linear, so a solution valid for a configuration of N spheres can be assembled from the superposition of individual solutions written in spherical coordinates about the origin of each sphere. Added to this solution is the external field (if any) imposed upon the spheres, such as a temperature gradient in the fluid. For the particular problem at

hand, the solution can thus be written

$$T_f = \nabla T_0 \cdot \mathbf{r} + \sum_{i=1}^{N_t} T_f^i \{r_i, \theta_i, \phi_i\}, \tag{21}$$

$$\mathbf{v} = \sum_{i=1}^{N} \mathbf{v}^i(r_i, \theta_i, \phi_i). \tag{22}$$

To formulate the boundary conditions on the surface of sphere i, the "partial" solutions written about all the other spheres in the configuration must be transformed into solutions written in spherical harmonics about i. This can be accomplished through use of an addition theorem for solid spherical harmonics, which can be written in the form

$$r_j^{-(n+1)} P_n^m \{\cos \theta_j\} e^{im\phi_j} = \sum_{l=0}^{\infty} \sum_{k=-n}^{n} A_{kl}^{mn} r_i^l P_l^k \{\cos \theta_i\} e^{ik\phi_i}, \quad R \geqslant r_i, \tag{23}$$

where the addition coefficient A_{kl}^{mn} is dependent only upon the distance and direction of translation from sphere j to i.

By substituting the addition theorem into the series expressions for the partial field, truncating the series, and applying the boundary conditions at each sphere, a linear relationship among the field expansion coefficients can be obtained. This relationship will be of the general form

$$\mathbf{a}^i + \sum_{\substack{j=1 \\ j \neq i}}^{N_s} [\mathbf{T}^{ji}] \mathbf{a}^j = \mathbf{f}^i, \tag{24}$$

where $\mathbf{a}^i$ represents the vector containing the field coefficients (either $(a_{mn}^i, b_{mn}^i, c_{mn}^i)$ or (d_{mn}^i), $\mathbf{T}^{ji}$ is a "translation" matrix from origin j to i, and $\mathbf{f}$ contains the boundary condition and external field information. Equation (24) written for each of the N spheres forms a complete system of linear algebraic equations for the field coefficients, which can be solved using appropriate iteration or elimination techniques.

Complete description of the thermophoretic behavior of the sphere configuration begins with the solution of the temperature field for a given external temperature gradient. This solution then supplies the thermal slip boundary condition in the creeping flow problem. The thermophoretic force and torque acting on each sphere, and the agglomerate as a whole, are obtained directly from the degree $n = 1$ expansion coefficients in the velocity field representations. The fluid resistance properties of the aggregate are characterized from the solution of the velocity expansion coefficients with boundary conditions representing aggregate motion and rotation in the fluid.

The thermophoretic behavior of two basic types of aggregates have been investigated using this formulation for the work presented here, namely, straight chains and relatively dense, randomly packed clusters. Results of the computations are summarized in Figure 2, in which $\alpha_T D$, calculated for continuum ($Kn = 0$) conditions and normalized with the value of a single primary sphere, are plotted vs the number of spheres in the aggregate, N. The ratio of the particle and gas thermal conductivities, k_g/k_p, was taken to be 0.1 for all calculations. Straight chain results are given for a gas temperature gradient parallel and perpendicular to the chain axis, and the random cluster results represent the average values computed for ten different configurations. The solid fraction of the clusters, based on the smallest sphere completely enclosing the cluster, was between 0.25 and 0.35.
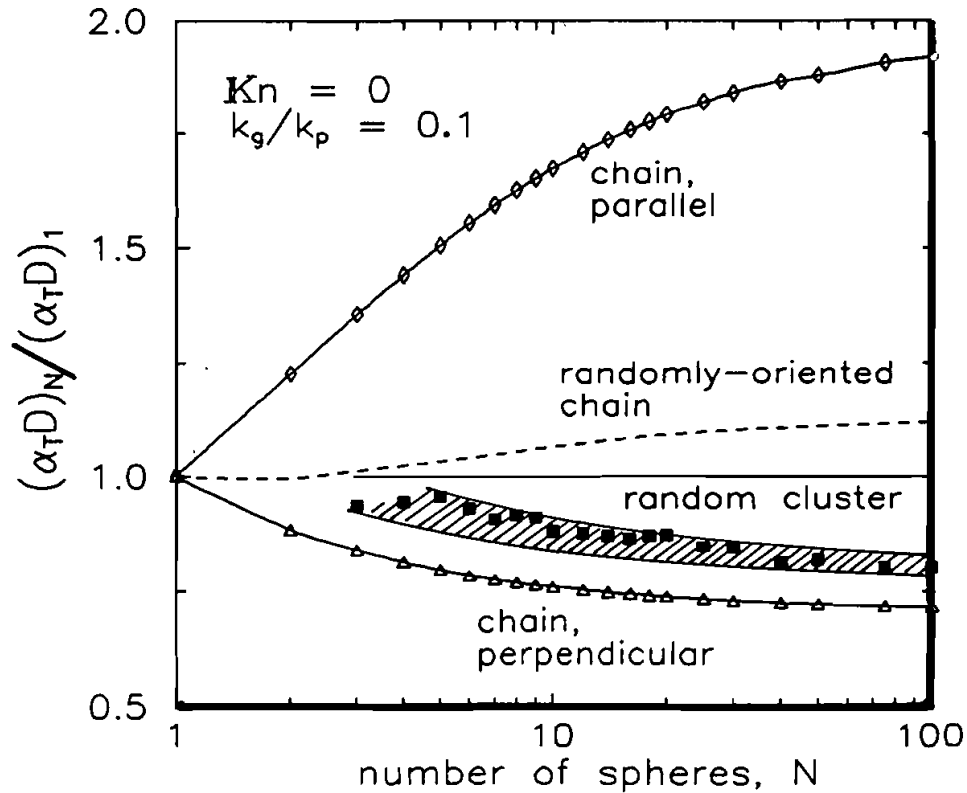
FIGURE 2   Predicted thermophoretic properties of linear- and quasi-spherical aggregated particles containing N primary particles in the continuum ($Kn \ll 1$) limit; thermal conductivity ratio $= 0.1$ (after Mackowski, 1991).

As expected, the parallel component of the chain $\alpha_T D$ is greater than the perpendicular component. In the limit of infinite chain length, the parallel and perpendicular components asymptote to approximately twice and two-thirds the value of a single sphere, respectively. The random-orientation-averaged value

$$\langle \alpha_T D \rangle = \tfrac{1}{3}(\alpha_T D)_{par} + \tfrac{2}{3}(\alpha_T D)_{per} \tag{25}$$

is thus around 10% larger than the single sphere $\alpha_T D$. The $\langle \alpha_T D \rangle$ values for the random clusters, on the other hand, are approximately 20% smaller than the single sphere results for large N.

It should be cautioned that in many environments *asymmetrical* aggregates will be formed and the assumption of random orientation may not be valid. Recent investigations (Mackowski (1990), Rosner *et al.* (1990)) have indicated that, for small aggregates of *non-identical* spheres, thermophoresis can result in an orienting torque on the aggregate. Such net torques will generally act to align the long axis of a straight chain aggregate with the prevailing gas temperature gradient, despite the counteracting tendency of Brownian rotation. Consequently, the *actual* orientation-averaged $(\alpha_T D)_N$ for a chain aggregate could be somewhat larger than the *random*-orientation value given above (*cf.* also, Figure 1, 2; curves marked "parallel orientation"). Of

course, for dense, quasi-spherical aggregates, thermophoretic alignment will have a less significant effect on $\langle \alpha_T D \rangle_N$.

2.3 Experimental Evidence

In several experimental studies of organic soot deposition on cooled targets (see, e.g., Eisner and Rosner, 1986, Makel and Kennedy, 1991) from atmospheric pressure flames, it has been reported that the thermophoretically dominated absolute deposition rates were in approximate agreement (say, $\pm 10\%$) with thermophoretic diffusivities estimated from Waldmann kinetic theory for small spherical particles. From our present viewpoint it is significant that this agreement occurs despite the fact that the soot prevailing in these flames, and being captured, was extensively aggregated. Moreover, in very recent experimental studies of the thickness of thermophoretically induced "dust-free" zones in $TiCl_4$-seeded laminar CH_4-N_2-O_2 counterflow diffusion flames (Gomez, and Rosner, 1991) it was concluded that the TiO_2 particles have $\langle \alpha_T D \rangle_N$-values within about 7% of the Waldmann (single sphere, $Kn \gg 1$) values. While the implications of this noteworthy agreement were not really addressed in any of these papers, we now believe that the explanation lies in the insensitivity of $\langle \alpha_T D \rangle_N$ to aggregate size, N, and morphology, which is the focus of this communication.

2.4 Analogies from the Electrophoresis of Colloidal Particles in Liquid Electrolytes

In the domain of colloidal particle phoresis in viscous fluids (see, e.g., Anderson, 1989) a noteworthy and interesting "precedent" is the electrophoretic drift of a "large" insulating particle in an unbounded Newtonian electrolyte. M. Smoluchowski in 1914 derived an expression for the electrophoretic velocity of an isolated spherical solid particle subjected to an imposed electrical field, and proposed that the result would hold for an insulating body of arbitrary size and shape provided that the fluid sublayer of nonzero net charge (the Debye sheath) adjacent to the surface is small on the scale of the local radii of surface curvature. This conjecture was supported by D. C. Henry in 1931, who also treated cylinders, and finally proven by Morrison, 1970. Under these same conditions, Reed and Morrison, 1976, showed that two identical spheres will move with the same velocity as one isolated sphere at all interparticle separations and orientations relative to the electric field. Very recently, Acrivos, et al., 1990, have proven that a "cloud" containing N identical spherical particles of arbitrary concentration but surrounded by an infinite expanse of particle-free liquid will move at the same velocity as a single isolated spherical particle. Moreover, these results also carry over to the surface-tension driven migration of bubbles or immiscible liquid droplets in a non-isothermal Newtonian host liquid. Indeed, from our present viewpoint it is interesting that the abovementioned analyses are based on the nonzero "slip velocity" at the outer edge of the Debye sheath induced by the local electrical field, which plays a role similar to the "thermal creep" velocity appearing in the near-continuum analysis of isolated particle thermophoresis in gases (see, e.g., Brock, 1962 and Mackowski, 1990, 1991). While it should be noted that aggregate particles comprised of touching spheres evidently do not satisfy the abovementioned local radius of curvature condition, these liquid phase "precedents" help explain the remarkable insensitivity we find of $\langle \alpha_T D \rangle_N$ to size and morphology for aggregates comprised of primary quasi-spherical particles in non-isothermal gases at $Kn \ll 1$.

3   ENGINEERING IMPLICATIONS

3.1   *Deposition Rate Predictions*

We have already noted (Section 2.3) that actual soot deposition rates from atmospheric pressure combustion gases to cooled solid targets can be predicted with remarkable accuracy using the thermophoretic diffusivity expected for the primary particles themselves, even though the actual soot aggregate sizes and morphologies are non-uniform and complex. Indeed, the insensitivity of aggregate $\langle \alpha_T D \rangle$ to size and morphology dramatically simplifies the task of making engineering predictions of soot deposition rates from flowing combustion gases, at least up to the level of shear stress necessary to cause deposited particle "re-entrainment" (Makel and Kennedy, 1990) or the inability of an arriving particle to "find a stable home" in the deposit (Konstandopoulos and Tassopoulos, 1990, 1991). It is now well known that thermophoretically dominated particle deposition rates from laminar boundary layers (Goren, 1977, Gokoglu and Rosner, 1984, 1986, Batchelor and Shen, 1985) and turbulent boundary layers (see, *e.g.*, Rosner and Fernandez de la Mora, 1982) are nearly proportional to the product $\langle \alpha_T D \rangle$, unless the mainstream particle loading is appreciable (Rosner and Park, 1988). Thus, the abovementioned size/structure insensitivity of the $\langle \alpha_T D \rangle$-value for aggregated particles, especially in the free-molecule limit but even in the near-continuum limit, translates directly into an insensitivity of soot deposition rates to the aggregate size/morphology distribution in the gas mainstream. In contrast, from our previous comments about the Brownian diffusivity $\langle D_N \rangle$ itself, and the fact that convective-diffusion deposition rates are nearly proportional to $\langle D_N \rangle^{2/3}$ in lightly-loaded systems, it follows that one can *not* make accurate predictions of convective diffusion-controlled soot deposition rates (*e.g.*, in nearly isothermal circumstances) without a detailed knowledge of the size- and morphology-distribution of the prevailing aggregated particles (see, *e.g.*, Rosner, 1991, and Rosner *et al.*, 1991). This size/morphology sensitivity will also be true in flow systems for which particle *inertia* plays an important role in determining deposition rates, as in the case of the flow of a particle-laden high speed fluid over solid bodies with streamwise curvature (Israel and Rosner, 1983, and Konstandopoulos and Rosner, 1990) or even turbulent flows over straight surfaces (see, *e.g.*, Rosner and Tassopoulos, 1989). This follows from the Einstein relationship: $\langle D_p \rangle = (k_B T / m_p) \cdot \langle t_p \rangle$, where $\langle t_p \rangle$ is the (orientation-averaged) particle stopping time, which plays a decisive role in determining the extent of dynamical non-equilibrium between the suspended particles of mass m_p and the accelerating/decelerating carrier fluid at local temperature T (see, *e.g.*, Rosner, 1986, 1990).

Returning to the case of thermophoretically-dominated aggregate deposition (the focus of the present paper), it should be noted that, whereas total mass deposition rates *can* be accurately estimated without a detailed knowledge of the aggregate size/morphology distribution, it will *not* be possible to predict the *deposit microstructure* (and, hence all microstructurally sensitive transport properties, including the effective thermal conductivity) without this additional information (Tassopoulos, O'Brien, and Rosner, 1989).

3.2   *Capture Efficiency Variations in Soot Particle Sampling*

On the plausible assumption that particle capture efficiency variations would be much smaller for thermophoretic sampling than for capture by Brownian diffusion or inertial impaction, Dobbins and Megaridis, 1987 have recently exploited and recommended this "intrusive" technique as an indispensable aid in studying soot dynamics

in hydrocarbon/air flames. They also indicated that their observed morphology distributions were insensitive to probe size. The transport evidence assembled and discussed here confirms their basic assumptions and indicates that relative populations of soot aggregates as seen on a lightly loaded cold electron microscope target cannot be very different from the relative aggregate populations existing in the combustion gas stream being sampled, especially for atmospheric- or subatmospheric-pressure flames. In the near-continuum limit our recent results for the modest size and morphology dependence of $\langle \alpha_T D \rangle$ (Figure 2, Section 2.2) combined with thermophoretic capture theory (see, e.g., Eisner and Rosner, 1986) would begin to allow systematic corrections to be made for the associated capture efficiency variations in the thermophoretic sampling process at higher pressures.

3.3 Size/Structure Insensitivity of $\langle \alpha_T D \rangle$ Compared to Size/Structure Sensitivity of Aggregate "Optical" Properties

Non-intrusive "optical" diagnostic techniques based on polarized light scattering and/or extinction are on firm ground in regions where the primary particles are spherical, homogeneous, widely separated and say, log-normally distributed with respect to size. However, in regions where the particles are extensively aggregated the interpretation of extinction and light scattering data becomes problematic, as recently demonstrated by Dobbins, Santoro, and Semerjian, 1991. These authors compared inferred soot area/volume-values based on the isolated sphere theory and a simplified quasi-fractal aggregate theory, revealing local differences of about a factor of three, and much larger differences in the corresponding inferred soot growth/oxidation rates.

Using transient thermocouple response techniques Eisner and Rosner, 1986 demonstrated that, in regions free of extensive "vapor growth" or heterogeneous oxidation (gasification), the laws of thermophoresis could be used to infer local soot volume fractions (and, indirectly, local gas temperatures) independent of assumptions regarding particle size spectra or optical properties. It now becomes clear that such local "immersion" methods are largely independent of the size/morphology of inevitable soot aggregates present in these regions, adding considerably to their attractiveness. Nonetheless, it is likely that *combinations* of optical techniques with careful sampling techniques will be necessary, and continue to bear fruit.

3.4 Consequences for "Dust-Free Zone" Thickness and Brownian Sublayer Thickness

A corollary of the findings discussed above is that the state of soot aggregation will not appreciably influence the boundary position of the so-called "dust free" zone near a hot solid surface (Park and Rosner, 1987, 1991, Friedlander *et al.*, 1988) or diffusion flame "sheet" (Gomez and Rosner, 1991).* However the thickness and internal structure of such a "front", being dictated by the (distribution of) Brownian diffusivities, *will* change appreciably with the degree of aggregation. Put another way, if one were trying to separate soot aggregates of different sizes and morphologies, thermophoretic means (without asymmetrical particle orientation using electric and/or magnetic fields) would not be particularly effective. The results shown in Sections 2.1–2.2,

---

*Zachariah *et al.* (1989), appear to conclude from their optically inferred silica particle diameter axial profiles that there is a broad spectrum of thermophoretically determined particle stagnation planes, spanning over a 1 mm distance depending upon particle size. This interpretation seems to us to be unlikely for the Knudsen numbers (O(1)) encountered in their silane-seeded hydrogen/oxygen experiments.

however, indicate that thermophoretic separation of *oriented* nonspherical aggregated particles, *e.g.* straight chains, remains feasible, and would be most effective in the near-continuum (high pressure) limit.

3.5 Conjectures Regarding Polydispersed Primary Particles, Tangential Momentum Accommodation, Particle Thermal Conductivity, and Intermediate Knudsen numbers

While the size distribution of the primary particles is quite narrow in many laminar systems with negligible backmixing (see, *e.g.*, Megaridis and Dobbins, 1990), in general one might find that the primary particles comprising the aggregates are themselves "polydispersed". This kind of spread is known to influence the drag behavior of linear chains of quasi-spherical primary inorganic particles—indeed, Kops *et al.*, 1975 and G. Kasper, 1982 have provided empirical formulae allowing this effect to be included in the estimation of linear chain aggregate capture by convection-Brownian diffusion or inertia. However, from the aggregate themophoresis results discussed in this paper for several important morphologies we conjecture that $\langle \alpha_T D \rangle$ for aggregates comprised of nonuniform size quasi-spherical particles will also be insensitive to the spread of the primary particle size distribution function, especially in the free-molecule limit. If confirmed by future research this feature will further simplify the engineering prediction of aggregate particle deposition rates in non-isothermal systems characterized by broad distributions of residence times.

Our recent results for the free-molecule limit (Garcia-Ybarra and Rosner, 1989) also suggest that the abovementioned size/structure insensitivity will be further improved when tangential momentum accommodation is *incomplete* upon gas/solid encounters with the primary particles. Indeed, we found that $\langle \alpha_T D \rangle$ is *independent* of sphero-cylinder particle aspect-ratio for the case of purely "specular"[*] gas molecule reflection. While the factors that determine the scattering properties of primary particle surfaces are not yet well understood (see, *e.g.*, the recent paper of Schaefer and Hurd, 1990), it appears that departures from the diffuse reflection limit will favor the size/structure insensitivity of $\langle \alpha_T D \rangle$. In the near-continuum limit, the same can be said for the effects of increasing particle thermal conductivity (Mackowski, 1991).

Finally, while we have not yet studied the intermediate Knudsen number regime, from the well-known size dependence of the single sphere $\alpha_T D$-value, we expect that sufficiently "compact" aggregates will have $\langle \alpha_T D \rangle$-values which fall off appreciably with N. However, it can be conjectured that sufficiently "open" or elongated aggregates will probably also have N-insensitive $\langle \alpha_T D \rangle$-values even when, say, the gas mean-free-path is comparable to the aggregate radius of gyration.

4   CONCLUSIONS, FUTURE WORK

Our recent calculations for a variety of canonical aggregate particle configurations and available experiments on soot transport from/in flames point to the following important simplification in treating the migration of aggregated particles through nonisothermal gases: *Due to a near-cancellation between incremental thermal force and incremental drag the orientation-averaged thermophoretic diffusivity* $\langle \alpha_T D \rangle_N$ *of*

---

[*]Since Waldmann's result for a single spherical particle contains the factor $[1 + (\pi \alpha_{mom}/8)]^{-1}$ it is known that thermophoretic velocities for the case of no tangential momentum accommodation (specular reflection) are greater than for the case of complete tangential momentum accommodation ("diffuse" reflection) by the factor of only $(1 + (\pi/8)) = 1.3927$.

aggregates comprised of N uniform sized primary particles is remarkably insensitive to aggregate size, N, and morphology, being within about 8% of the value for a single primary particle in the free-molecule limit and within about 21% of the value for a single primary particle in the continuum limit. It is reasonable to expect that this result will also hold if the primary particles are themselves not uniform in size, and even in the Knudsen transition regime unless the primary particles are "tightly packed". It follows that the reported size/morphology insensitivity of $\langle \alpha_T D \rangle_N$ will often allow sufficiently accurate engineering predictions of total mass deposition rates (Rosner, 1989) to cooled targets based only on a knowledge of the *total soot volume fraction* in the mainstream; moreover, our present conclusions support the efficacy of thermophoretic soot sampling methods (see, *e.g.*, Dobbins and Megaridis, 1987) and thermophoresis-based probes of local soot volume fraction and gas temperature (Eisner and Rosner, 1986), as well as the inefficiency of aggregate size/morphology separation by thermophoretic means unless the aggregates are asymmetrical and orientation-averaging (*via* Brownian rotation) can be prevented.

Future research will be necessary to better define the limits of validity of these conclusions and conjectures, and extend the presently cited calculations to include other important aggregate morphologies and, ultimately, intermediate Knudsen numbers.

ACKNOWLEDGEMENTS

REFERENCES

Acrivos, A., Jeffrey, D. J., and Saville, D. A. (1990). Particle Migration in Suspensions by Thermocapillary or Electrophoretic Motion. *J. Fluid Mechanics* 212, 95–110.

Anderson, J. L. (1989). Colloid Transport by Interfacial Forces. *Ann. Rev. Fluid Mechanics* 21, 61–99.

Batchelor, G. K. and Shen, C. J. (1985). *J. Colloid Interface Sci.*, 107, 21–37.

Brock, J. R. (1962). On the Theory of Thermal Forces Acting on Aerosol Particles. *J. Colloid Sci.* 17, 768–780.

Dobbins, R. A. and Megaridis, C. M. (1987). Morphology of Flame-Generated Soot As Determined by Thermophoretic Sampling. *Langmuir (ACS)* 3, 254–259.

Dobbins, R. A. and Megaridis, C. M. (1991). Optical Cross-section of Soot Aggregates. *Applied Optics* (in press).

Dobbins, R. A., Santoro, R. J., and Semerjian, H. G. (1991). Analysis of Light Scattering From Soot Using Optical Cross-Sections for Aggregates. *23rd International Combustion Symposium*, The Combustion Inst. (Pittsburgh PA), 1525–1532.

Eisner, A. D. and Rosner, D. E. (1985). Experimental Studies of Soot Particle Thermophoresis in Non-Isothermal Combustion Gases Using Thermocouple Response Techniques. *Combustion and Flame* 61, 153–166.

Eisner, A. D. and Rosner, D. E. (1986). Experimental and Theoretical Studies of Submicron Particle Thermophoresis in Combustion Gases. *J. PhysicoChemical Hydrodynamics* (Pergamon Press), 7, 91–100.

Friedlander, S. K., Fernandez de la Mora, J., and Gokoglu, S. A. (1988). Diffusive Leakage of Small Particles Across the Dust-Free Layer Near a Hot Wall. *J. Colloid & Interface Sci.* 125, 351–355.

Garcia-Ybarra, P. and Rosner, D. E. (1989). Thermophoretic Properties of Nonspherical Properties and Large Molecules. *AIChE. J.*, **35**, 139–147.

Gokoglu, S. A. and Rosner, D. E. (1984). Correlation of Thermophoretically Modified Small Particle Diffusional Deposition Rates in Forced Convection Systems With Variable Properties, Transpiration Cooling, and/or Viscous Dissipation. *Int. J. Heat Mass Transfer* **27**, 639–645.

Gokoglu, S. A. and Rosner, D. E. (1986). Thermophoretically-Augmented Forced Convection Mass Transfer Rates to Solid Walls Across Non-Isothermal Laminar Boundary Layers. *AIAA J.* **24**, 172–179.

Gomez, A. and Rosner, D. E. (1991). Thermophoretic Effects on Particles in Counterflow Laminar Diffusion Flames. (In preparation); see also, Paper 26f 1987 AlCkE Meeting, New York City.

Goren, S. L. (1977). Thermophoresis of Aerosol Particles in the Laminar Boundary Layer on a Flat Plate. *J. Colloid & Interface Sci.*, **61**, 77–85.

Happel, J. and Brenner, H. (1965). Low Reynolds Number Hydrodynamics. Prentice-Hall, Englewood Cliffs, NJ.

Israel, R. and Rosner, D. E. (1983). Use of a Generalized Stokes Number to Determine the Aerodynamic Capture Efficiency of Non-Stokesian Particles from a Compressible Gas Flow. *J. Aerosol Sci. & Tech.* **2**, 45–51.

Kasper, G. (1982). Dynamics and Measurement of Smokes II. The Aerodynamic Diameter of Chain Aggregates in the Transition Regime. *Aerosol Sci. Tech.* (*Elsevier*), **1**, 201–215.

Kim, S. and Karrila, S. J. (1990). Microhydrodynamics: Principles and Selected Applications. Butterworths-Heinemann, Stoneham, MA.

Konstandopoulos, A. G. and Rosner, D. E. (1991). Inertial Effects on Thermophoretic Transport of Small Particles to Walls With Streamwise Curvature-I. Experiment, II. Theory. (Prepared for submission to *Int. J. Heat Mass Transfer*).

Konstandopoulos, A. G. and Tassopoulos, M. T. (1990). Simulation of Particle Impaction: Sticking Probability and Microstructure Evolution in the 'Frozen' Deposit Limit. *1990 Annual Meeting of the Amer. Assoc. Aerosol Research*, Philadelphia, PA. Paper 6E.6.

Konstandopoulos, A. G. and Tassopoulos, M. T. (1991). A Kinetic Model of Deposit Growth: I. Characterization of Particle Sticking Probability. *1991 AIChE Annual Meeting*, Los Angeles, CA.

Kops, J., Dibbets, G., Hermans, L., and Van de Vate, J. F. (1975). The Aerodynamic Diameter of "Branched" Chain-Like Aggregates. *J. Aerosol Sci.*, **6**, 329–333.

Leong, K. H. (1984). Thermophoresis and Diffusiophoresis of Large Aerosol Particles of Different Shapes. *J. Aerosol Sci.*, **15**, 511–517.

Mackowski, D. W. (1987). Investigation of the Radiative Properties of Chain-Agglomerated Soot Formed in Hydrocarbon Diffusion Flames, *PhD. Dissertation*, U. Kentucky.

Mackowski, D. W., Altenkirch, R. A. Menguc, M. P., and Saito, K. (1988). Radiative Properties of Chain-Agglomerated Soot Formed in Hydrocarbon Diffusion Flames. *22nd International Combustion Symposium*, The Combustion Institute (Pittsburgh PA), 1263–1269.

Mackowski, D. W. (1990). Phoretic Behavior of Asymmetric Particles in Thermal Nonequilibrium with the Gas: Two-Sphere Aggregates. *J. Colloid & Interface Sci.* **140** (1), 138–157.

Mackowski, D. W. (1991). An analysis of the Thermal and Hydrodynamic Properties of Aggregated Spheres in the Near-Continuum Regime. (To be submitted).

Mackel, D. B. and Kennedy, I. M. (1991). Experimental and Numerical Investigation of Soot Deposition in Laminar Stagnation Point Boundary Layers. *Proc. 23rd International Combustion Symposium*, The Combustion Inst. (Pittsburgh PA), 1551–1557.

Mason, E. A. (1957). Higher Approximations for the Transport Properties of Binary Gas Mixtures: II. Applications. *J. Chem. Phys.* **27**, 782.

Megaridis, C. M. and Dobbins, R. A. (1990). Morphological Description of Flame-Generated Materials, *Combustion Sci. Tech.* **71**, 95–109.

Morrison, F. A. (1970). The Electrophoresis of a Particle of Arbitrary Shape. *J. Colloid & Interface Sci.* **34**, 210–214.

Park, H. M. and Rosner, D. E. (1987). Thermophoretically Induced Phase Separation in Highly Mass-Loaded 'Dusty' Gas Mixtures. Yale Univ., HTCRE Lab. Public. No. 162.

Reed, L. D. and Morrison, F. A. (1976). Hydrodynamic Interaction in Electrophoresis. *J. Colloid & Interface Sci.* **54**, 117–133.

Rosner, D. E. and Fernandez de la Mora J. (1982). Small Particle Transport Across Turbulent Non-Isothermal Boundary Layers. *ASME Trans-J. Engrg. for Power*, **104**, 885–894.

Rosner, D. E. (1986, 3rd printing 1990). Transport Processes in Chemically Reacting Flow Systems, Butterworth-Heinemann, Stoneham, MA.

Rosner, D. E. (1989). Total Mass Deposition Rates from "Polydispersed" Aerosols, *AIChE. J.* **35**, 164–167.

Rosner, D. E. (1989a). Side-wall Gas "Creep" and "Thermal Stress Convection" in Microgravity Experiments on Film Growth by Vapor Transport. *Physics Fluids A-Fluid Mechanics* **1**, (11), 1761–1763.

Rosner, D. E. (1991). Particle Size- and Structure-Sensitivity of Total Mass Deposition Rates from Streams Containing Coagulation-Aged Populations of Aggregated Primary Particles. (In preparation).

Rosner, D. E. and Park, H. M. (1988). Thermophoretically Augmented Mass, Momentum and Energy Transfer Rates in High Particle Mass-Loaded Laminar Forced Convection Systems, *Chem. Engrg. Sci.*, **43**, 1497–1508.

Rosner, D. E. and Tassopoulos, M. (1989). Deposition Rates from "Polydispersed" Particle Populations of Arbitrary Spread, *AIChE. J.* **35**, 1497–1508.

Rosner, D. E., Mackowski, D. W., Tassopoulos, M., Castillo, J., and Garcia-Ybarra, P. (1990). Effects of Heat Transfer on the Dynamics and Transport of Small Particles in Gases. Paper 293e Presented at the (S. W. Churchill Birthday) Symposium: *Advances in Rate Processes*. AIChE 1990 Annual Meeting, Chicago IL, November 12, 1990; *Industrial and Engineering Chemistry-Research* (ACS) Special Issue (in press, 1991).

Rosner, D. E., Konstandopoulos, A. G., Tassopoulos, M., and Mackowski, D. W. (1991). Deposition Dynamics of Combustion-Generated Particles: Summary of Recent Research Studies of Particle Transport Mechanisms, Capture Rates and Resulting Deposit Microstructure/Properties, *Proc. Engineering Foundation Conference*: Inorganic Transformations and Ash Deposition During Combustion (in press); see, also: *Proc. 7th Annual DOE-PETC Coal PUEC Contractor's Meeting* (July 15–18, 1991).

Schaefer, D. W. and Hurd, A. J. (1990). Growth and Structure of Combustion Aerosols—Fumed Silica, *Aerosol Science and Technology*, **12**, 876–890.

Smoluchowski, M. V. (1914). Handbuch der Elektrizitat und des Magnetismus, (L. Graetz, ed.), Vol. 2, Barth, Leipzig.

Tassopoulos, M., O'Brien, J. A., and Rosner, D. E. (1989). Simulation of Microstructure/Mechanism Relationships in Particle Deposition, *AIChE. J.* **35**, 967–980.

Ulrich, G. D. and Richl, J. W. (1982). Aggregation and Growth of Submicron Oxide Particles in Flames, *J. Colloid & Interface Sci.*, **87**, 257.

Ulrich, G. D. and Subramanian, N. S. (1977), Particle Growth in Flames—III. Coalescence as a Rate-Controlling Process. *Comb. Sci. and Tech.*, **17**, 119–126.

Waldmann, L. and Schmitt, K. H. (1966). Thermophoresis and Diffusiophoresis of Aerosols, Chap. 6 in *Aerosol Sci.* (C. N. Davies ed.), Academic Press, London, 137–162.

Williams, M. M. R. (1986). Thermophoretic Force Acting on a Spheroid, *J. Physics D, Applied Physics* **19**, 1631–1642.

Williams, M. M. R. (1987). The Thermophoretic Forces Acting on a Bispherical System, *J. Physics D, Applied Physics*, **20**, 354–359.

Zachariah, M. R., Chin, D., Semerjian, H. G., and Katz, J. L. (1989). Dynamic Light Scattering and Angular Dissymmetry for the *In Situ* Measurement of Silicon Dioxide Particle Synthesis in Flames. *Appl. Optics*, **28**, 530–536.